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THE EMISSION OF RADIATION IN CHEMICAL REACTION.

A THESIS.

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INTRODUCTION.

The description of the occurrences in the series of elementary processes which constitute most of the events observed in the physical world is a problem, the initial attempts to solve which are warranted by the progress made in the development of atomic theory. In chemistry it has been possible to draw the outlines of the conventional picture which we may regard as representing the material changes occurring in reactions by connecting the known facts of chemical combination with the conceptions arrived at by physicists with regard to the structure of atoms; but a similar attempt to visualise the manner in which the elementary energy changes occur would seem to require, on account of the absence of corresponding generalisations on this side of the problem, special experimental investigation.

According to current views, the material changes in chemical reactions consist essentially in a re-arrangement of the outer electrons surrounding the kernels of the interacting atoms. The formation of a heteropolar compound consists in the transference of electrons belonging to the more electropositive constituent to the more electro negative; in sodium chloride, for example, the single valency electron of the sodium atom has been more or less transferred to the chlorine atom, with the formation of a system both of whose constituent atoms contain the distribution of electrons which the periodic occurrence of the inert gases in the table of the elements appears to indicate to be the most stable.

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The formation of homopolar compounds also involves the entrance of electrons, which before reaction were associated wholly with one atom, into the configuration of another; though here the process is one of the sharing of electrons rather than of their transference from one atom to another.

Now, the phenomena of the emission and absorption of light are ascribed to the motions of electrons in matter; the reactions of matter on light, reflection, refraction, dispersion, and so on, are also caused, at least for light of short wavelength, by the motion of electrons. In particular, the emission of the series lines produced by the passage of electricity through gases and in other ways has received at the hands of Bohr and of his followers an explanation which, enables us, granting their postulates, to form a quite coherent picture of the processes occurring. Briefly, the essential part of the explanation is that radiation is emitted, not in the process of the vibration of an electron in a stable orbit, but in the passage of the electron from one to another of a discreet system of orbits, the frequency ν of the emitted radiation being determined by the relation

$$E = h\nu$$

where E is the difference in the energy of the atom in the respective states, and h is Planck's constant.

There is thus a similarity between the processes which/

which are supposed to occur in chemical reactions and in the emission of radiation by matter, and the question arises whether chemical reactions may be accompanied by the emission of radiation as an essential part of the event.

The effect of the absorption of light in originating chemical change is known from the study of photochemical reactions. In a photochemical reaction, whether on the whole it involves an increase or a decrease of free energy, the stage which is light-sensitive must take place with the absorption of energy; and that this absorption in the specific photochemical process takes place in quanta is shown by experiments undertaken to test Einstein's Law of Photochemical Equivalence to be extremely probable. The absorption of one quantum, it appears, in the simplest case, will cause the absorbing molecule to undergo the primary photochemical reaction, provided it is of sufficient magnitude to effect the change. For example in the photochemical combination of hydrogen and bromine, Warburg [Sitz.d. kon.preusz.Akad. 1916, p.314] assumes the primary light reaction to be dissociation of bromine molecules;

$$Br_2 + h\nu = Br + Br.$$

The recombination of Br atoms is an exothermic reaction, the reverse of the photochemical reaction, and just as the decomposition of the molecule may be effected by the absorption of light of definite frequency, so, it might appear, the recombination of the atoms may take place with the emission of the same radiation.

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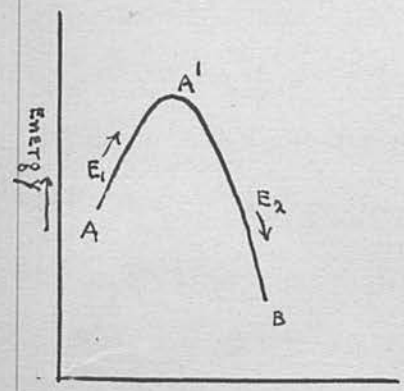
The general radiation theory of chemical reaction of Lewis and of Perrin, particularly in theform developed by Perrin [Ann.de.Physique [IX] II,5 (1919); Trans. Far.Soc.17,3,(1922)] requires, from a somewhat different point of view, that the energy made available in a reaction should appear primarily as radiation. According to this hypothesis, the reaction A→B takes place thus: the initial system A is capable of reacting only if it attains a state A' with which is associated a definite quantity of energy; this state is reached by the absorption of an amount E_1, of radiant energy, present in th e system in virtue of its temperature in thermal reactions, imposed from without in photochemical reactions. The condition A' is not one of permanent stability; its behaviour is determined by unknown laws, but th e final result, according to the hypothesis, is that it either reverts to the original condition A, with the emission ,as radiation, of energy E_1, or it assumes the condition B with the emission of energy E_2 also as radiation. If the energy of the system in the condition B is less than that in A, there will be a tendency for the reaction to preceed in the direction A → B,and the observed change in total energy for the reaction/



reaction will be $E_2 - E_1$. The quantities E_1 and E_2 may be called the "critical increments" of the reactants and resultants respectively.

The interesting experiments described by Perrin on the fluorescent light emitted by certain organic substances [Ann .de.Phys. [IX] 10, 133 (1918)] in which he claims that fluorescence involves the destruction of the fluorescing molecule and is emitted at the moment of destruction, and therefore represents the emission stage in his scheme of the course of reaction, involve reactions in wh ich the energy changes are too little known to form a quantitative test of the theory, even if his conclusions remained unchallenged. [See Wood, Phil.Mag. [VI] 43,757 (1922); Pringsheim, Z.f. Physik, 10,178, (1922)] The quantitative development of the radiation hypothesis has been chiefly along the line of the calculation of the velocity of reaction, and especially of determining the significance of the temperature coefficient of the velocity, and most reactions studied have had to subscribe to the condition that they must possess an easily measurable velocity: in these reactions the energy changes are usually comparatively small, and any radiation would be emitted at low frequency, in the infra red. To test the question it seems desirable to choose as simple reactions as possible, inwhich moreover the energy changes are sufficient to cause any emission as high frequency radiation/

radiation.

Many reactions are known to take place with the emission of light, which however, does not appear to be a primary emission of the energy of reaction as radiation. A feature of many reactions which are accompanied by the emission of radiation is their very high velocity; if the conditions are so modified that the velocity is lowered, visible emission often ceases, although there may still be a sufficient amount of reaction to cause a considerable evolution of energy as heat. The light emitted in such reactions therefore does not seem to be an essential part of the process, but rather a secondary effect, associated with high reaction velocity. This does not imply that the light emitted is purely the result of the high temperature prevailing; it is certain that the luminosity of many flames cannot be accounted for by such a hypothesis. The manner in which such emissions may originate will be discussed later.

The formation of heteropolar compounds seemed to be the kind of reaction in which any emission of the energy of reaction as radiation would be most readily detected, and the halogens were chosen as the electronegative components. The purpose of this work was therefore to find if such reactions as the formation of the halogen hydrides and of the halides of the alkali metals were accompanied by the emission of radiation/

radiation which could be correlated with the possible energy changes taking place in the reaction. If the emission of the energy of reaction is a quantum process, the frequency of the radiation, provided that the emission occurred as one quantum, would be given by the equation $E=h\nu$ where E is the elementary energy change. This will not, in general, be equal to the observed heat of reaction, which is, except possibly in the very simplest reactions, the nett result of a member of consecutive changes occurring in the reaction. The formation of hydrogen chloride, for instance, from gaseous chlorine and hydrogen under ordinary conditions must be a complex process, involving the dissociation of Cl_2 and H_2 as well as union to HCl; but from thermo-chemical data it is possible to calculate the energy change E in possible elementary processes, as the union of atomic hydrogen and atomic chlorine, and from the equation $E=h\nu$ determine the region of the spectrum in which chemical radiation might be expected. Even this value of E would, according to the notions of the course of chemical changes derived from the study of reaction velocities, be a composite quantity, being the difference between the "critical increments" of resultants and reactants which are the true elementary energy changes. It has been observed, however, that reactions which take place with high velocity are associated with low critical increments of the reactants; hence it is likely that for such reactions as the formation of the alkali/

alkali halides which take place, at least in the absence of extreme dryness, with high velocity, the heat of reaction calculated for the union of metal and halogen atoms will be nearly equal to the energy emitted in the elementary process. For most reactions in which heteropolar compounds are formed, the corresponding wavelength is, as will be shown in the discussion of th e individual cases studied, in the ultra violet, so that the absence of visible emission is no argument against the case that chemical radiation may be produced in these reactions, and special experiment is necessary to decide the question.

A knowledge of the ultraviolet spectra of the halogens seemed desirable, since they act as the receiver of the electron in the chemical reaction, and in the first part of the work the radiation emitted by these elements on electrical excitation was studied. Then the emissions caused by the passage of the electric discharge through the hydrides and through the vapour of a metallic halide were examined; this was followed by the study of some specific reactions. Also experiments suggested by the results of the investigation of the spectra of the halogens, were performed on the effect of high frequency ultraviolet light on iodine vapour.

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The Emission Spectra of the Halogens.:

Although many communications have appeared on the spectra of the halogen s, they have been confined, for the most part, to the visible or near ultra violet regions. The emission spectra of chlorine and bromine down to about $\lambda = 370 \mu\mu$ have been described by Eder and Valenta [Beiträge zur Photochemie, pp 358, 369 (1904)] as consisting of lines, chiefly in the green and blue. For bromine, besides the line spectrum a continuous emission was also observed beginning in the green; at about $420 \mu\mu$ a second continuous band appeared and extended with increasing intensity to the limit of their photograph at about $370 \mu\mu$. These spectra were produced by passing a powerful spark through the gases at relatively high pressure.

Iodine in particular shows many interesting phenomena in its optical behaviour; it is one of the few gases which have been found to emit radiation on mere heating to such moderate temperatures as 500° to 700° C; it exhibits to a marked degree the property of emitting light previously absorbed as fluorescent and resonance radiation; and, correspondingly, its spectrum under various conditions of excitation has occupied the attention of several investigators. [Konen; Ann. der Physik 65, 257, (1898); Wood, Researches in Physical Optics, part ii, p. 51 (1919)] With the exception, however of some results* which have appeared during the course/

* Stenbing: Ann.d, Physik 64, 673, 1921 visible sp. of I.
Angerer Z.f. Physik II, 167, 1922; u.v. band sp. of Cl.
Z.f. wiss. Phot. 22, 200, 1923, u.v. line of Cl.
Jevons Proc. Roy. Soc. A, 103, 193, 1923, u.v. line sp of Cl
Gerlach and Grommann, Z.f. Physik, 18, 239, 1923, u.v. band spectrum of I.

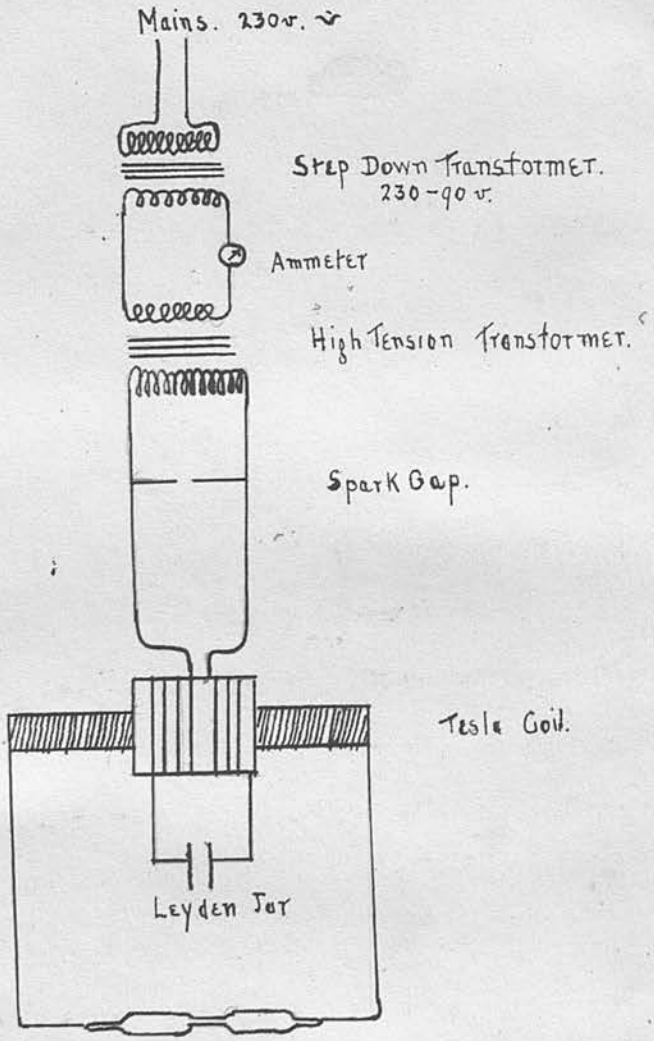
course of this work or just ~~the~~ previous to its commencement, little was known of the emission spectra of the halogens in the further ultraviolet region, and special investigation became necessary.

Procedure: The tubes were constructed of clear fused silica; the use of cement was thus avoided, with the possibility of introducing traces of impurity. As appeared in the course of the work, the spectra of the halogens are extremely susceptible to disturbance in the presence of traces of impurities, and every means must be taken to avoid them.

The discharge tubes consisted of 2 bulbs, IO cm. long and I.5 cm. in diameter, joined axially by a capillary. Round the outside of the bulbs were tightly wound strips of tinfoil, fixed in position by coating the seams with rubber solution. These served as electrodes.

Electrical Arrangements: The discharge was obtained from a small Tesla coil, constructed as described by Drude [Ann. der Physik, 8, 336, (I902)] The primary consisted of two coils, each of 3½ turns of stout copper wire wound on a/ cardboard former supported on ebonite pillars; the diameter of the coils was 6 inches. The coils were connected respectively to the inner and outer coatings of a Leyden jar of a capacity 0.005 μF. The secondary, of 300 turns of silk insulated wire, wound on a former 2 inches in diameter, was inserted within the primary; the diameters of the formers were so chosen that no spark passed between the primary and secondary/

FIG. I – Electrical Arrangement.



secondary coils. A large induction coil, worked from a IO volt battery, was first used to drive the Tesla, but this was later replaced by a high tension transformer which could be run, on occasion, with IO amps. at 230 volts in the primary, giving IO,000 volts in the secondary. In most of the observations, this was worked from a step-down transformer, which reduced the supply voltage from 230 to 90, and the current in the primary of the high tension transformer was usually about 3amps. The secondary of the high tension transformer was connected to an aluminium spark gap, to which the primary of the Tesla was joined. The electrical arrangement is shown in fig. I .

The action of the electric system is briefly as follows: Opposite coatings of the condenser in parallel with the spark gap become charged from the secondary of the high tension transformer, and discharge takes place through the primary of the Tesla and the spark gap as a high frequency oscillatory discharge, the frequency varying inversely as the square root of the capacity. An oscillatory current of this very high frequency is induced in the secondary of the Tesla; the two sets of coils of the Tesla also act as a step up transformer, so that the potential difference between the terminals of the secondary is very high. The currents are correspondingly low, so that there is no danger of puncturing the tubes, as happened sometimes when the induction coil was directly attached to the discharge/

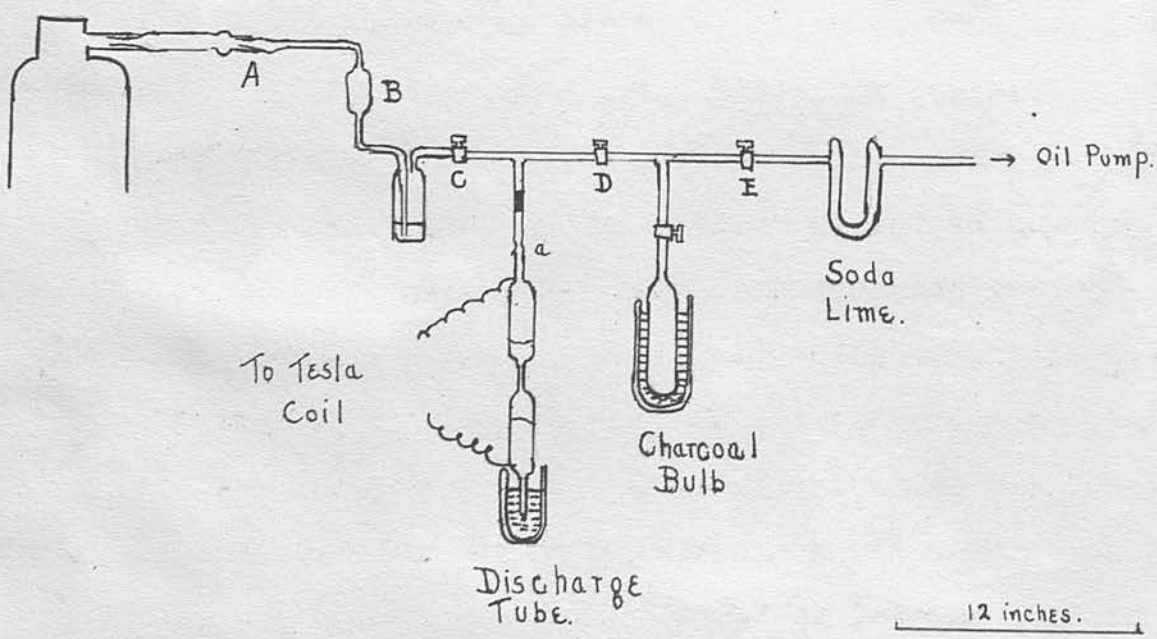
discharge tube, and the current can be passed for long periods without causing serious rise in the temperature of t he tube.

Filling the Tubes: It was soon found that special care must be taken to obtain the gases free from impurity. Attempts to obtain Chloriné tubes by long continued passage of the gas through the tube and evacuation to a suitable pressure were comparative failures. The spectra of the tubes thus obtained showed that considerable quantities of air were present. Finally a tube whose spectrum was nearly free from impurity was obtained by the use of liquid air.

Chlorine: The gas was obtained from a commercial cylinder. A wide piece of glass tubing was drawn down so as to slip inside the carefully cleaned iron outlet of the cylinder, and the joint was secured by rubber passing over the glass and iron. Only by diffusion along the joint bet ween the glass and iron could the chlorine come in to contact with the rubber. A_1 (fig 2) was a ground glass joint, un lubricated but made vacuum tight externally by means of Everett Vacuum Wax. The gas was dried by concentrated sulphuric acidcontained in a wash bottle with sealed in inlet and outlet, and with a trap B to prevent the sucking back of acid to the cylinder. The discharge tube was connected by a rubber joint flush with the end of a glass T piece; all other joints were made by grinding or by fusing. To the T piece was fused a bulb containing cocoa nut charcoal.

FIG. 2.

FILLING OF CHLORINE TUBE.

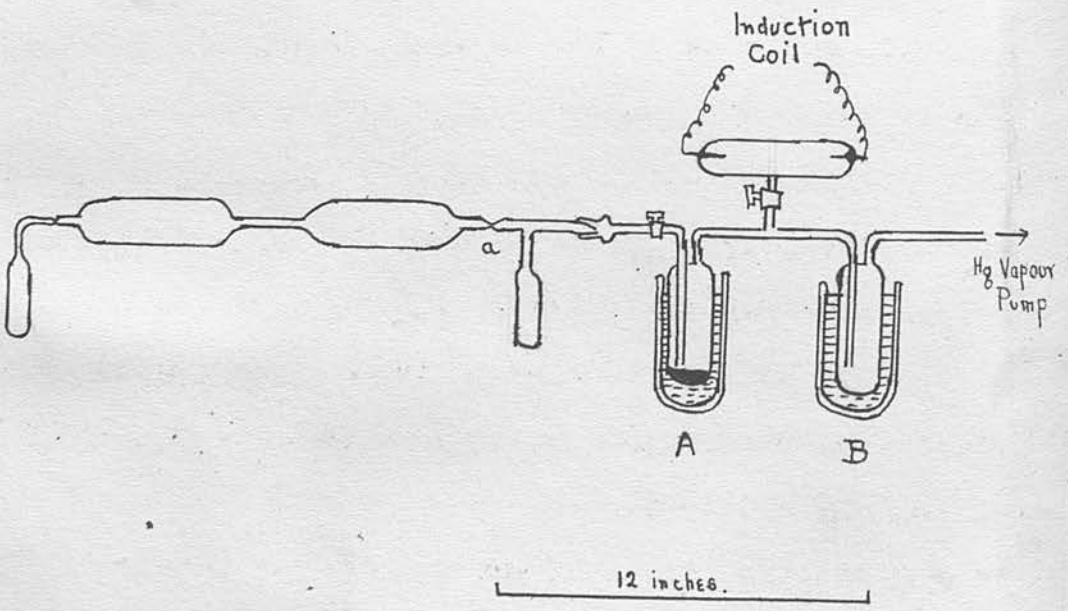


charcoal; this was connected through a soda lime tube to a rotatory oil pump, capable of yielding a vacuum of 0.001 mm. A shortened form of McLeod Gauge, with range from 5 to 0.001 mm. proved convenient for determining the degree of evacuation; this was protected by absorbents from the action of the halogen.

The lower portion of the discharge tube was immersed in liquid air, and a large quantity of chlorine collected in it as a nearly white solid. The tap C was then closed and the apparatus up to this point evacuated to as low a pressure as possible by means of the oil pump; after which tap E was closed and the charcoal bulb immersed in liquid air. The charcoal, the discharge tube, and connecting tubes had previously been strongly heated in vacuo over the naked flame in order to remove moisture and occcluded gases. Evacuation by the charcoal cooled in liquid air was continued for half an hour, so that the pressure of air left must have been excessively small. The liquid air was then removed from below the discharge tube and most of the chlorine allowed to distil into the charcoal bulb, which was still cooled in liquid air. Liquid chlorine having disappeared from the discharge tube, tap D was closed and the pressure in the tube gradually reduced by manipulating D until a bright glow was obtained on starting the Tesla. The silica tube was then sealed off at the constriction a by means of the oxygen coal gas blowpipe/

FIG. 3.

FILLING OF BROMINE TUBE.



blowpipe flame.

A chlorine tube was also filled at atmospheric pressure, and the pressure reduced by cooling in liquid air so as to allow the passage of a discharge. By adjusting the temperature it was thus possible to observe the variation of the appearance of the discharge with pressure.

Bromine: A satisfactory bromine tube was obtained only after many unsuccessful attempts. Several tubes prepared with the help of charcoal-liquid air evacuation showed impurity lines quite strongly, although the quantity of impurity was so small that, if the bromine was frozen out by means of liquid air, scarcely any emission of radiation took place on passing a current, and a photographic plate exposed in the spectrograph for an hour was unaffected; yet, on allowing the pressure of bromine to rise so that a bright glow was emitted on electrical excitation, air lines were prominent in the resulting spectrum.

A satisfactory tube was eventually obtained with the help of a mercury vapour condensation pump, backed by a rotatory oil pump. Silica bulbs were fused to either end of the discharge tube, as shown in fig 3. Bromine, previously shaken with concentrated potassium bromide solution, dried with concentrated sulphuric acid, and finally distilled over phosphorus pentoxide and solid potassium bromide, was introduced into the bulb remote from the pump. The connection between the discharge tube/

tube and the pump was made by a ground silica to glass joint, not lubricated, but made vacuum tight by sealing with vacuum wax. Rubber was entirely avoided. A and B were traps immersed in liquid air, A containing mercury to prevent access of halogen to the pump; B to prevent the diffusion of mercury vapour from the pump to the small test discharge tube introduced for the purpose of estimating the vacuum. The bulb containing the bromine was immersed in liquid air and the apparatus evacuated until no discharge passed in the test tube. The tap was now closed, and the bromine allowed to distil backwards and forwards between the silica bulbs, connection being made to the pump after each distillation to remove any air dissolved in the bromine. The tube was sealed off at "a" containing solid bromine in the first tube, immersed in liquid air. At the time of sealing, no discharge would pass in the tube. The bulb containing the bromine was immersed in alcohol at -60°C, and sealed off, so that the pressure of the vapour in the tube was $\frac{1}{3}$ mm. One tube was sealed off containing liquid bromine, so that it was possible by regulating the temperature, to observe the appearance of the discharge at different pressures.

Iodine: Iodine tubes were easily prepared by subliming a small quantity of pure iodine into the discharge tube, evacuating as far as possible with the oil pump, and completing the evacuation by attaching to charcoal immersed in liquid air. No difficulty was experienced/

experienced with impurities.

Effect of Impurities: This effect, in which it seems that at total pressures of the order 0.I to Imm. the relative number of molecules of impurity, such as air or carbon compounds, excited to emission is much greater than the relative number of halogen molecules so behaving has been noted by nearly all previous workers on the spectra of the halogens; to avoid it, Eder and Valenta (Beiträge zur Photochemie, p.362) were compelled to use pressures from I to IO cm. The relative intensities of the spectral emissions of the components of a gaseous mixture depend on complicated and imperfectly known laws, but one of the chief determining factors will be the relative ease with which the different constituents are ionised. In a gaseous mixture, the gas with the lowest ionisation potnetial will most readily carry the current. The ionisation potentials of bromine and of chlorine are not satisfactorily known, but they are practically certainly greater than those of the oxygen or/the gaseous carbon compounds; oxygen is ionised by ultraviolet light transmitted by fluorite, while chlorine is not appreciably ionised by this radiation.* [Ludlam, Phil.Mag. (VI) 23, 757, (I9I2)]. In the case of iodine, whose ionisation potential is certainly below those of oxygen or nitrogen (IO volts compared with I6 volts for oxygen/

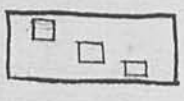
* The only work on the critical potentials of chlorine and bromine have been done by Hughes and Dixon (Phys.Rev. IO, 495, I9I7), who report a critical potential for chlorine of 8.2 volts, and for bromine at IO volts. The method used does not distinguish between ionisation and radiating potentials, and it is certain that these figures are not the ionisation potentials of the substances.

oxygen and 17 volts for nitrogen), there was no intrusion of impurity lines in the spectrum, although there is no reason to suppose that the quantity of air present in the tube was absolutely any less than in the bromine or chlorine tubes.

Photography of the Spectra: A small Hilger quartz spectrograph was used, which gave th e region from 800$\mu\mu$ to 180$\mu\mu$ within the compass of a quartz plate. The dispersion in the visible was very small; the region from 650 to 390$\mu\mu$ being crushed into a length not much more than 2 cm. The mean dispersion between 400 and 300$\mu\mu$ was about 6$\mu\mu$ per mm; between 300 and 250$\mu\mu$ about 3$\mu\mu$ per mm.; below 250$\mu\mu$ the dispersion increases very rapidly as the absorption band of quartz is approached, being at 200$\mu\mu$ nearly 1$\mu\mu$ per mm.

Ilford Special Rapid Panchromatic plates were employed; these plates have a minimum of sensitiveness in the green, a fact which has to be borne in mind in considering the intensity of the photograph in this region. The visible spectrum was always checked by visual examination through a direct vision spectroscope.

For the purpose of measuring the plates, the spectra of the halogens were bracketed by metallic spark spectra, generally of zinc or aluminium. Above the slit of the spectrograph was was placed a cover provided with three holes as shown, which were brought



one after the other over the slit. The spectrum of the halogen was photographed through the cen tral hole, the

compar ison/

comparison spectra through the others.

The wavelengths were estimated from a large scale graph obtained by plotting the wavelengths of known metallic lines against their distance from a fixed point on the plate. For approximate determinations a scale of wavelengths was constructed from a photograph of the spark between a zinc and a cadmium electrode. There may be an error of about I $\mu\mu$ in the region between 300 $\mu\mu$ and 400 $\mu\mu$; between 300 and 250 $\mu\mu$ measurments mey be relied on to less than 0.5 $\mu\mu$, and at 200 $\mu\mu$ they are probably correct to 0.I $\mu\mu$. Naturally, under these conditions of accuracy the wavelengths ar e not reduced to their values in vacuo.

Appearance of the Glow: At pressures of about 5 mm. the glow in chlorine was bluish white and concentrated, passing straight between the electrodes and not filling the tube. At higher pressures the current passed as a spark. At about I mm. the glow was a brilliant bluish white, completely filling the tube. As the pressure was lowered, the colour changed to white, became feeble, and finally at pressu res of about $\frac{1}{100}$ to $\frac{1}{1000}$ mm. disappeared.

The glow in bromine showed a similar behaviour. At a pressure of 30 mm., the discharge passed as a purplish spark. With diminishing pressure, the glow gradually filled the tube, and remained purplish to a pressure of about 5 mm.; it then became white, till at pressures/

pressures below 0.I mm. it turned to bright yellow,

The iodine glow at 0.I mm. was very brilliant bluish white; on lowering the pressure it became first a bright, and then a dull yellow, finally disappearing.

Although these colour changes were very pronounced, neither visual observation through the direct vision spectroscope nor the photographic plate showed any great change in the character of the spectrum. The eye appears to be much more sensitive in detecting variations in the nett effect of a number of colours than in observing changes in the individual colours.

Phosphorescence of the Tubes: A remarkable feature of these discharges was the brilliant and persistent phosphorescence of the quartz. The phosphorescent glow was much increased on warming the tube; portions thus excited to emit more intensely than surrounding portions lose the property more rapidly than the latter. After all visible glow had ceased at the ordinary temperature, which usually took place in about half and hour or less, the quartz could be excited to bright phosphorescence by warming; on one occasion, heating the tube five days after the passage of a discharge caused the glow to flash up brilliantly for a short time, and the effect has been observed a fortnight after a current was passed. The phosphorescent glow became much less intense when the gas pressure in the tube was low, and ceased when the pressure was too low to allow the production/

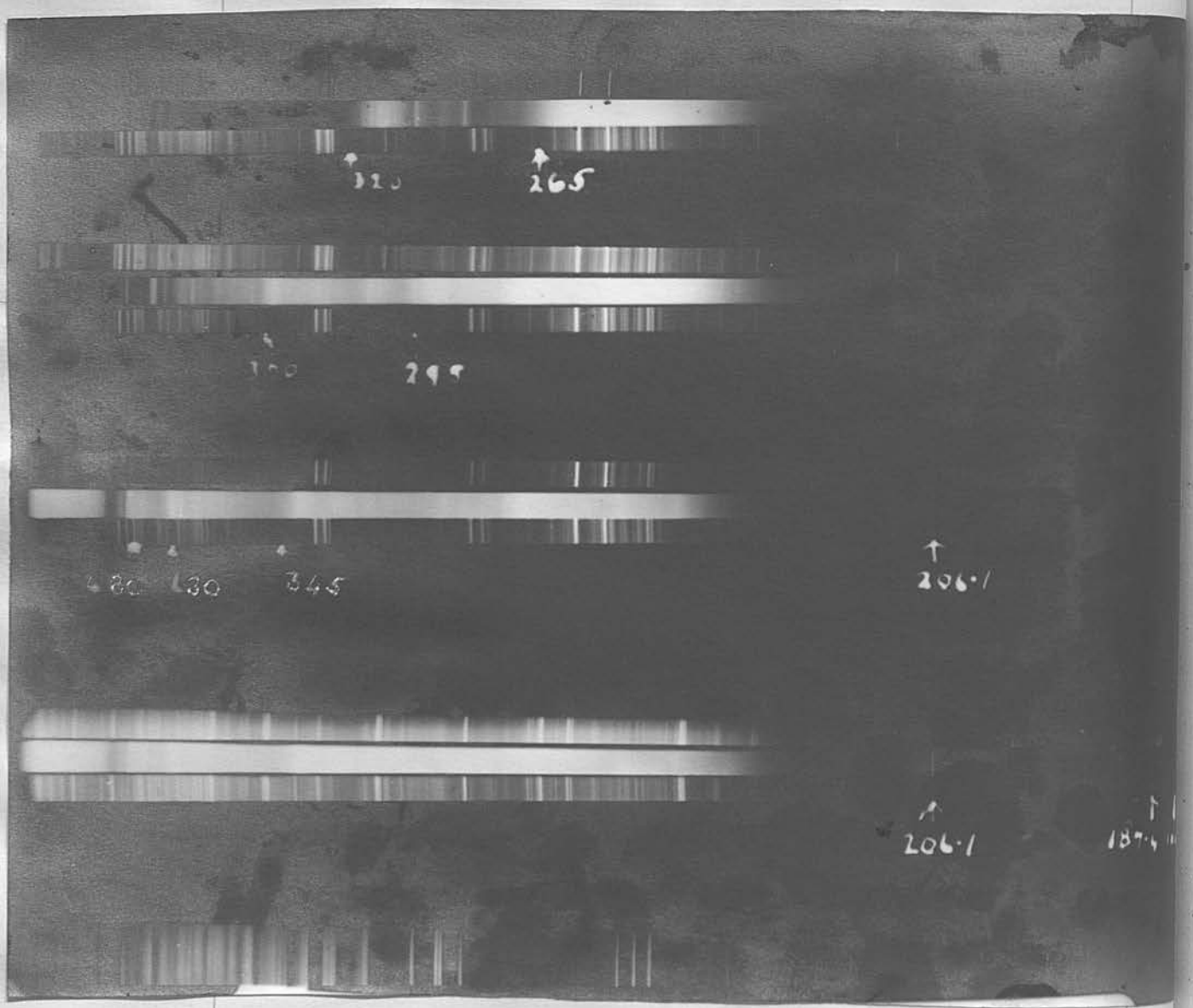
production of a visible glow in the gas. The light, which was usually brilliant green, does not appear to be due primarily to the quartz, but rather to traces of impurities contained in it, for with one tube, made by joining two silica bulbs obtained from the manufacturers at different times, the colour in the one bulb was the usual intense green, while in the other it was a pale blue. It was found that exposure of fused silica to radiation from the aluminium spark caused the same phosphorescence; as in this case it cannot be due to an electrical effect, nor to the impinging of molecules on the walls, it seems most probable that the phosphorescent glow in the dischargetube is also brought about by ultraviolet radiation emitted by the gas.

The effect was not obtained to any extent in tubes containing air, but hydrogen tubes gave a very intense phosphorescence. Hydrogen emits a great number of strong lines at about 160$\mu\mu$, and also the Lyman series commencing at about 120 $\mu\mu$; the aluminium spark has groups of intense lines at 185 $\mu\mu$; for iodine, a series of strong lines has been found whose first member is at 206 $\mu\mu$, followed by others in the further ultra violet; for bromine and chlorine, it seems probable, from their relations to iodine as shown in the less refrangible parts of the spectrum, that a corresponding series will exist in the very short ultraviolet, beyond the region examined in this work; on the other hand, no lines or bands/

FIG. 4.

EMISSION SPECTRA OF THE HALOGENS -

(Enlarged from ¼-plate.)



The Zinc spark-spectrum forms the comparison in the first three photographs, the Aluminium in the fourth. The spectra, from the top downwards, are of Cl, Br, I, I (long exposure), Air.

bands have been observed for oxygen between 200 and I23 μμ , while nitrogen bands in this region are faint , [Lyman, Spectroscopy of the Extreme Ultra-violet, p.82] so that there appears little doubt that the phosphorescence is produced in the quartz by the action of radiation of shorter wavelength than about 200 μμ . According to the views of Lenard and Klatt [Ann.d.Physik I6, 63I, (I904)], the emission of phosphorescent light is produced by the return to the phosphorescent centres of electrons previously ejected, as in the photoelectric effect, by the action of the radiation; the great persistence of the glow at ordinary temperature may be associated with the high insulating power of quartz, which will cause the return of the electrons to be slow, and the increase in brightness but less persistence at higher temperatures with the increase in the conductivity of quartz with temperature.

Results:

Chlorine: A very faint continuous emission commences at about 480 μμ and continues into the ultraviolet. In the reproduction, the intensity of this band is much greater in comparison with those in the ultraviolet than in the negative. At 320 μμ a strong continuous band begins and attains a maximum at 307 μμ. It then diminishes in intensity rather suddenly, but continues towards the further ultraviolet. At 265 μμ the most characteristic band in th spectrum commences; it rapidly attains a maximum at 260 μμ , falls off rather sharply at about 250 μμ , and then gradually decreases in intensity to about 230 μμ , where the absorbtion of the gelatine/

gelatine begins to cause a rapid decrease in the density of the image. These bands differ from ordinary band spectra in that they seem to be, as far as can be ascertained by the dispersion employed, perfectly continuous. All the chlorine spectra obtained show lines in the less refrangible portion; they are chiefly due to air, but include lines not present in theair spectrum, which are presumably due to chlorine. The chief of these are at 359 and 303 $\mu\mu$, which agree with the position of known chlorine lines. The quantity of air in the tubes was in all cases quite inadequate to give rise to a glow when the halogen was frozen out by liquid air, but in the presence of chlorine or bromine certain air lines appear. The effect of halogen in inducing the emission of radiation by the constituents of air is not equally shown by all wavelengths; for instance, the air spectrum contains characteristic group of four intense lines or narrow bands at 297, 289, 288, and 282 $\mu\mu$, of which the two at 297 and 282 persist in all chlorine and bromine spectra obtained. The middle pair, however, although the most intense in the spectrum of pure air, was always very feeble in comparison with the others in presence of halogen.

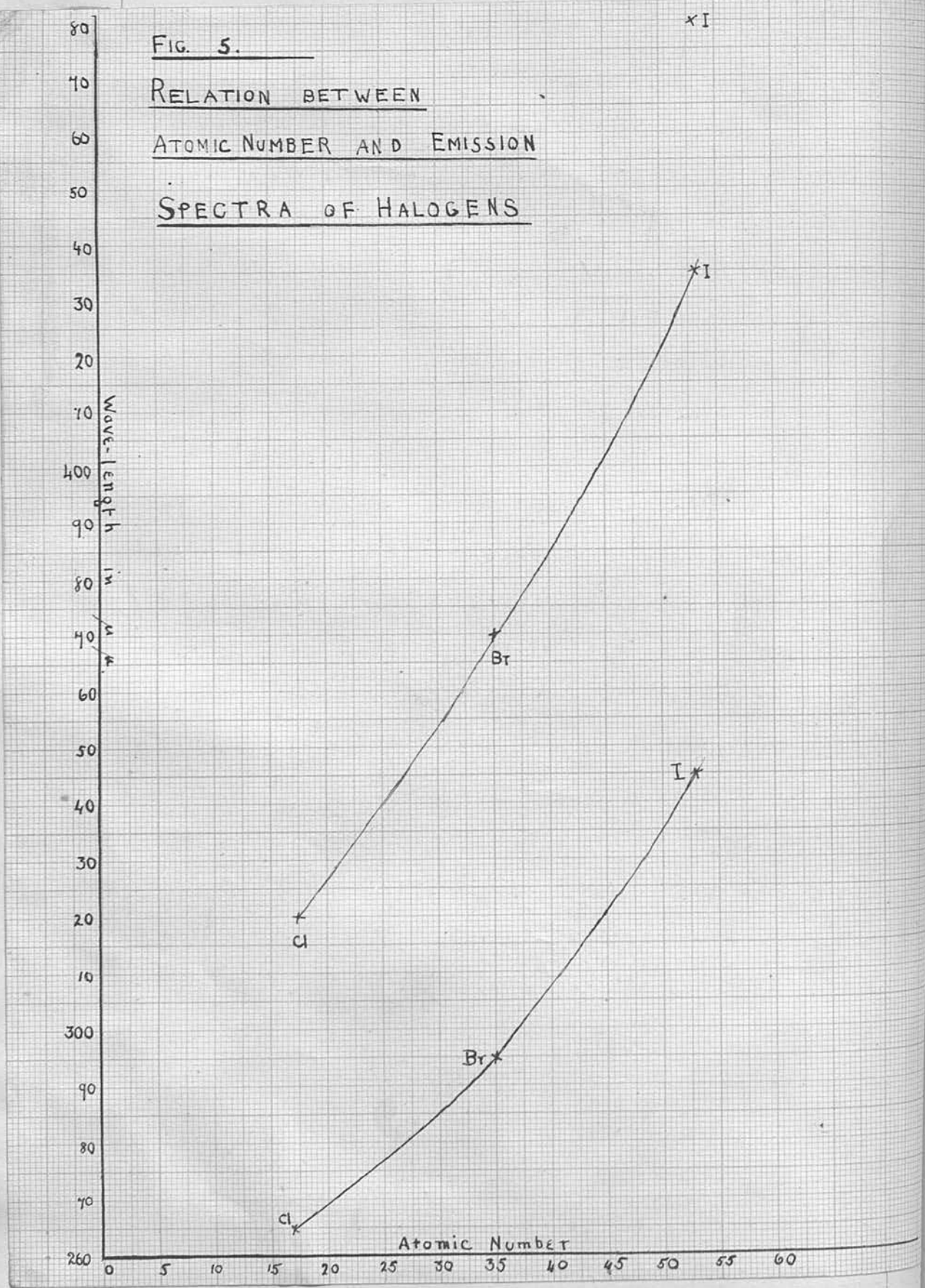
Bromine: A faint continuous band begins sharply at 420 $\mu\mu$. A strong band, which appears to correspond to the chlorine band at 320 $\mu\mu$, occurs at 370 $\mu\mu$, and a weaker/

weaker at 310 μμ. At 295 μμ begins the continuous band, which, from its brightness and the sharpness of its rise, appears to correspond to the chlorine band at 265 μμ ; the maximum is at 288 μμ after which it gradually decreases in intensity. The lines again, are chiefly due to air.

Iodine: While this work was in progress, a communication on the spectrum of iodine appeared from Gerlach and Grommann [Z.f.Physik, I8, 23 , (1923)] ; their results are confirmed, and in addition a new line spectrum has been observed in the limit of the region which can be examined without the use of a vacuum spectrograph. In the red-yellow-green region occurs the well known band spectrum with a sharp violet limit at 510 μμ ; the dispersion does not permit the resolution of the individual bands. Between the limit of this band and 480 μμ is a region in which the plate is only slightly affected; this is crossed by a number of lines characteristic of iodine, particularly by a pair in the blue at about 490 μμ. The photographic plate has a minimum of sensitivity in this region, but that there was an actual objective diminution in the intensity of the light emitted in this region by the iodine was shown by visual examination of the spectrum. A continuous band begins at 480 μμ and rapidly attains a maximum; another strong band begins at 430 μμ which is followed by subsidary maxima/

FIG. 5.

RELATION BETWEEN ATOMIC NUMBER AND EMISSION SPECTRA OF HALOGENS

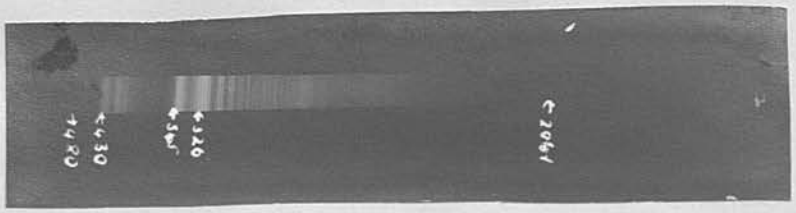


maxima of regularly decreasing intensity and distance apart. At 345 $\mu\mu$ the band begins which corresponds to the second continuous band of chlorine and bromine. This is continuous, and has a maximum at 342, beyond which it rapidlt falls off in intensity, although blackening is visible on the negative to nearly 200 $\mu\mu$. There is a faint group of bands, apparently of the ordinary band type with separate lines, degraded towards the ultra violet, at about 270 $\mu\mu$; and other groups are present at 248 and 237 $\mu\mu$. These latter groups are not well shown either in the negative or inthe reproduction.

It is not immediately obvious which of the continuous bands iodine emits at 480 $\mu\mu$ and at 430 $\mu\mu$ corresponds to the first strong band of bromine and chlorine, but the graph showing the relation between the long wave limits of the continuous bands and the atomic number of the radiator appears to answer the quest ion. Fig. 5 shows this relation. The 265 $\mu\mu$ band of chlorine the 295 $\mu\mu$ band of bromine, and the 345 $\mu\mu$ band of iodine lie on one smooth curve, while the 320 $\mu\mu$ chlorine band, the 370 $\mu\mu$ bromine band, and the 430 $\mu\mu$ iodine band lie om another, not quite parallel to the first. The 480 $\mu\mu$ band of iodine is off th e curve, and it appears that the 430 $\mu\mu$ band of this element corresponds to the first strong continuous band of the other halogens. This curve shows the essential similarity between the spectra of the three elements.

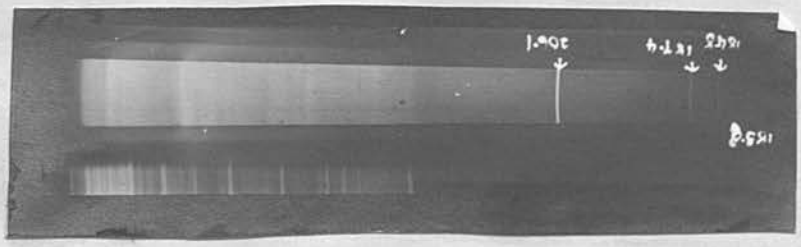
Besides/

FIG. 6.



The Iodine Spectrum at low current density.
The system of bands crossing the continuous band is well marked.

FIG. 7



The Ultra-violet Line-Spectrum of Iodine.

Four lines, of wavelengths 206·1, 187·4, 184·8, and 183·8 $\mu\mu$ are shown.

This photograph was taken on the fastest plate obtainable (Imperial Eclipse Speed No. 660 H & D) which was coated with a thin layer of, paraffin oil just before exposure. The faintness of the lines in an ordinary plate is largely due to the absorption of the gelatine of the plate. Paraffin oil also absorbs, but it re-emits the light as fluorescence radiation of larger wavelengths, not absorbed by the gelatine. In this way the absorptive action of the gelatine is evaded.

Besides showing these features in common with the other halogens, the spectrum of iodine contains a number of special features. Between 326 and 293 μμ a number of narrow bands appear, which seem to belong to a definite system. The first group contains several bands commencing on the red side at 326 μμ ; then follow four pairs at regularly decreasing distances, the separation between the members of each pair being about 2 μμ . This system is most prominent when very low currents are passed through the tube, as is shown in fig. 6 ,which was photographed when the spectrum was excited by a current induced in the Tesla coil by the high tension transformer not directly connected to the coil. These narrow bands appear to be identical with a group described by McLennan in the ultraviolet fluorescence spectrum of iodine vapour excited by the radiation of a quartz mercury lamp [Proc.Roy.Soc. 88 A, p.296] and hence are almost certainly emitted by the molecule. The group of bands just described is followed by a number of broader, hazy bands.

At 206.1 μμ the iodine spectrum contains a very sharp line, whose position is given accurately by the zinc line at 206.2 μμ ; three other fainter lines can be detected still further in the ultraviolet; their wavelengths, found with reference to the lines of the aluminium spark, are 187.4, 184.8, and 183.8 μμ . These fig. 7. lines must be intrinsically of very considerable intensity/

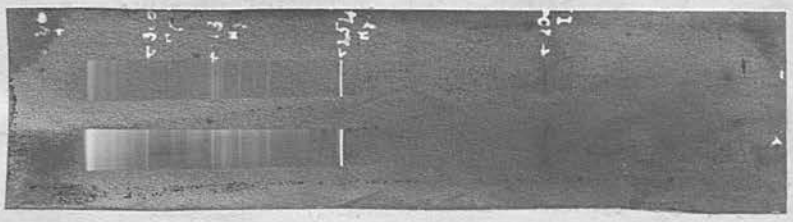
intensity, since both the gelatine in the photographic plate and the quartz tubes absorb largly in this region; moreover the oxygen of the air begins to absorb strongly at about 185 $\mu\mu$. These lines are perfectly sharp, and therefore must originate in the atom. The iodine used was carefully resublimed so that it could have contained no metallic impurity; the most likely impurity would be some of the other halogens, but since these give no such line, they are not responsible for the emission in iodine. The line likewise cannot belong to silicon excited to emission by the passage of the current through a volatile halogen, since there would have been at least as much probability of th e formation of such a compound when the tube contained bromine or chlorine. The only possible conclusion is that the line spectrum is due to the iodine atom. The ionisation potential of this atom is given as about 8 volts [Smythe and Compton, Phys. Rev. 16, 501, 1920] corresponding to a wavelength of about 150 $\mu\mu$, which will be the short wave limit of a line series, and it is probable that the 206 $\mu\mu$ line is the first member of this series. It will therefore be the resonance line of the iodine atom, produced by the removal of an electron from the normal orbit to the next of greater energy and its return to the first orbit, and will correspond to the D lines of sodium, ot the mercury lines at 254 $\mu\mu$ and 185 $\mu\mu$.

The band spectra of the halogens described here appear/

as
appear to,be the same spectra excited by the action of active nitrogen on these elements. [Strutt and Fowler, Proc.Roy.Soc. 86 A, 108, I ~~II~~] These authors reported that the passage of active nitrogen produced in a discharge tube over the halogens generated the emission of band spectra by these elements. For iodine; the strongest bands commenced at 343 $\mu\mu$ and at 477 $\mu\mu$; these obviously correspond to,the iodine bands at 345 and 480 $\mu\mu$. The iodine line at 206 $\mu\mu$ also appears to have been excited in this way, though their estimate of the wavelength, 207.5 $\mu\mu$ is somewhat different from that given here. For bromine and chlorine, only the second band was reported, at 293 and 260 $\mu\mu$ respectively, compared with the values 295 and 265 $\mu\mu$ found here. There is probably no real discrepancy between the wavelengths reported for the bands by Strutt and Fowler and those given here, as those authors probably measured the position of maximum intensity, while the values given here refer to the long wavelength limits of the bands.

Attempts were made to excite the iodine line at 206 $\mu\mu$ in other ways than by the passage of a current through iodine vapour at low pressure. The line was observed faintly in the spectrum of the light emitted when a spark was passed in air between metallic terminals in which holes had been drilled and filled with iodine. No iodine bands appear in these circumstances. The line also appears when an electric discharge is passed through the vapour of mercuric iodide at ordinary/

FIG. 8.



Spectrum of the glow-discharge in HgI_2 vapour. The 254 $\mu\mu$ Hg line is relatively much more intense in comparison with the other Hg lines than in the ordinary arc spectrum of Hg. The I line at 206 $\mu\mu$ appears faintly.

ordinary temperature in a vacuum tube (fig. 8); but two hour's exposure to the oxy-coal gas flame coloured with potassium iodide, and nine hours to the bunsen flame containing potassium iodide failed to show th e line; nor has it been observed in the spectrum emitted by a flame containing iodine nor by iodine vapour at low pressure up to 1000 mm. contained in a quartz tube heated to bright redness.

Comparison between the ultraviolet emission and absorption spectra of th e halogens:

A comparison of emission and absorption spectra affords one of the means whereby conclusions maybe reached as to the manner in which the spectra originate. The absorption spectrum of a substance, as ordinarily observed, is a result of processes affecting it in its normal condition; if then an emission spectrum proves identical with an absorption spectrum the conclusion may be drawn that it is due to the substance in the form which is normal under the particular conditions in which the absorption spectrum was observed. Many emission spectra, however, do not coincide with absorption spectra as ordinarily observed; the Balmer series for hydrogen, for instance, has no counterpart in the absorption spectrum of ordinary hydrogen. The absorption spectrum of hydrogen gas is a process affecting diatomic molecules; but the Balmer series is emitted by hydrogen which is quite abnormal. In the first place/

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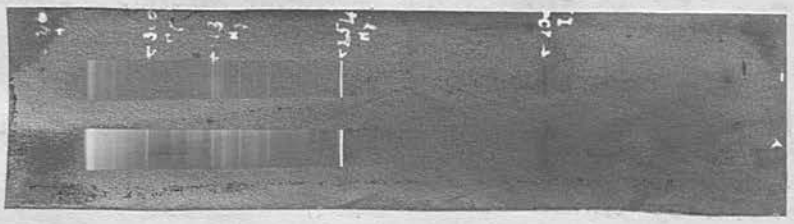

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place, the radiating entities are atoms, and not molecules; and in the second, they are abnormal atoms, in the sense that the emission is brought about by the return of an electron to an orbit of total quantum number 2 and not 1, in which the electron vibrates in the normal atom. In such cases no relation will exist between the ordinary absorption spectrum and the emission spectrum; the Balmer lines are obtained as an absorption series only by use of hydrogen excited by the passage of an electrical discharge, [Hulbert, Phys. Rev. 23, 593, (1924)] and their occurrence as absorption lines in stellar spectra indicates that hydrogen is present in the stars/from a terrestrial point of in what is view, an ab normal condition. It is, in fact, owing to the fortunate circumstances that in the case of the vapours of the alkali metals, the most readily observed emission spectrum originates in the normal atom, that it was possible to formulate the relation between absorption and emission, which gave the key to the explanation of the Fraunhofer Lines. In many other substances it is well known that coincidence between absorption and emission spectra fails, and in such cases one can assume that the emission originates in centres which in some way have been disturbed from their normal condition.

The following table contains details of the absorption/

absorption bands noted by different observers * and the long wave limits of the chief emission bands observed in these experiments.

Table I.

Halogen	Absorption		Emission	Absorption	Emission
	Extent	Maximum			
Iodine	550–430	490	480, 430	360–beyond 220	345
Bromine	530–340	420	370	280– " "	295
Chlorine	410–270	338	320	None in this region	265

There is no relation between the forms of the emission and the absorption bands. The emission bands are characterised by relatively sharp edges on the long wave side. while the absorption bands are not ~~so~~ well marked on either side. In every case the head of the first continuous band is contained in a region in which the halogen absorbs under normal circumstances, but too little is known about the quantitative nature of the absorption bands to warrant any conclusion concerning the origin of the emission band on this ground alone. The case is very different from/

* Living and Dewar, Proc.Roy.Inst, 10, 245, 1883, visible and u.v.sp.of Cl, Br. I.
Mrs Laird, Astrop.J. 14, 85, 1901; visible absorption of Cl, and var.with pressure.
Evans, Astrop.J. 32, 2 I, I 10; absorption of Br & I and variation with temperature,
Dobbie & Fox. Proc.Roy.Soc. A, , 460, I 21, visible absorption of halogens, and var.with temp.
St.Landeau-Ziemecki, Phil.Mag. 44, 651, I 22; absorption of I and variation with temp.
Coehn & Stuckhardt, Z.phys.Chem. 91, 733, 1916, u.v.absorption of halogens and their hydrides.
Rebaud; Ann.de Phys. 12, 135, 1919; photometric study of absorption of Cl and Br.
v.Halban & Siedentopf; Z.phys.Chem. 103, 71, 1923; quantitative absorption of chlorine.

from that of the red-yellow-green band of iodine, which is reproduced in nearly all its details both in emission and absorption spectra, so that there is no doubt that they originate from the same vibrating system, which must be the normal molecule; but for the first continuous ultraviolet band, although there is, to some extent identity in position of the emission and absorption spectra, it cannot be said that the forms in any way resemble one another.

The second continuous emission band of the three halogens takes place definitely in a region where there is practically no absorption of the normal vapour, and therefore is evidently not connected with any process occuring in the normal molecule.

Absorption of the Iodine Line at 206·1 μμ:-

If the line ~~is~~ observed in iodine at 206·1 μμ is the first member of the principal series, it ought to be absorbed by iodine atoms, since the first member of the primary absorption series is due to an electron suffering a quantum jump from the orbit of lowest energy to the first orbit of higher energy permitted by the selection principle of Rubinowicz and Bohr. A preliminary experiment had shown that the iodine line at 206·1 μμ was considerably weakened when the light from an iodine tube was passed through a column of iodine vapour at about ½cm. pressure heated in a hot bunsen flame, but not when the light was passed through the same column containing the same amount of vapour heated to 65°, the temperature required to maintain the vapour pressure of iodine at about/

about ½ cm. This indicates that the iodine atoms produced at the high temperature absorb the line at 206.1 μμ. Just then, the question was settled more conclusively bu Füchtbauer, Waibel and Holm [Z. fur. Physik, 29, 367, 1924] who obtained a sharp absorption line in iodine at 900°C at wavelength 206 μμ, using a powerful zinc spark as source. This confirms the original conclusion that the line is the first in the principal series of the iodine atom; it appears to be analogous to the sodium doublet at 589 μμ or the mercury line at 254 μμ which occur both as emission and absorption lines.

Discussion of the Spectra:

Note on Conversion Formulae: In the subsequent discussions it will often be necessary to express energy interms of the corresponding wavelengths as determined by the quantum theory, an d of the voltage through which an electron has dropped. The following conversion formulae were employed in the calculations.

I, To express wavelengths in terms of calories per gm. mol.

Each molecule absorbs a quantum $h\nu$, so that the energy absorbed by a gm. mol. is

$E = N h\nu$, E is in ergs. N is Avogadro's Number

If E is measured in kilogram-calories (Cals.) and the wavelength λ in μμ, we have

$$1000\ J\ E = \frac{N h\nu}{\frac{\lambda}{10^7}}$$

where J = Joule's equivalent, 4.18×10^7 ergs per cal.
N = Avogadro's Number, 6.062×10^{23}
h = Planck's constant 6.55×10^{-27}
V = velocity of light 3×10^{10} cm. per sec.

The factor 10^7 arises since 1 cm. = 10^7 μμ.

Hence

$$E(\text{in Kil. cal.}) = \frac{28490}{\lambda\ (\text{in } \mu\mu)}$$

(2) To express volts in terms of wavelengths: The energy of an electron which has fallen through a potential difference V electrostatic units is eV ergs, e being the electronic charge. If on collision with an atom, this electron parts with its energy, thereby effecting a change in the atom which can just be brought about by the absorption of a quantum of radiation of frequency ν, then $e V = h\nu$.

If V is in volts, and λ in $\mu\mu$, then since I volt $= \frac{10^8}{c}$ e.s.u.,

$$V \text{ (in volts)} = \frac{h \times \nu^2}{\frac{e \times \lambda \text{ (in } \mu\mu) \times 10^8}{10^7}}$$

$e = 4.774 \times 10^{-10}$ e.s.u. and v is again the velocity of light, so that,

$$V \text{ (in volts)} = \frac{1233}{\lambda \text{ (in } \mu\mu)}$$

(3) To express Kil.cals.per gm.molecule as volts per molecule.

N effective electronic collisions will be required to produce a change in I gm.mol. so that the energy required is N e V ergs where e and V are in electrostatic units.

$$= \frac{N e V \times 10^8}{1000 J v.} \text{ Kil.Cal.} \quad \text{where V is in volts}$$

$$E \text{ (in Kil.cals.)} = 23.1 \times V \text{ (in volts)}$$

The characteristic features of the spectra of the halogens observed in this work are the bands, which are continuous as far as can be seen with the dispersion employed. This was small, but use may be made of the results of Steubing [Ann.d.Physik, 64, 693, 1921] who found/

found that the iodine band at 480 $\mu\mu$ appeared continuous even at dispersions which completely resolved the very narrow band spectrum in the red-yellow-green region; and on analogy it may be concluded that the bands of the other halogens are continuous. A basis on which an interpretation of these halogens bands may be attempted may therefore be found in a consideration of the kinds of continuous spectra which have been observed.

Continuous absorption spectra are known commencing at the short wave limit of the principal series of the alkali metals, and continuous emission and absorption bands appear in the spectrum of hydrogen at the limit of the Balmer series. [Stark, Ann. d. Physik. 52, 255, 1917] The elementary theory of these bands has been given by Bohr. In the quantum theory of spectra, the last line of a series is emitted by the return of an electron, which has just been completely removed from an atom, to the positive residue. This line is indistinguishable from the continuous spectrum which begins at the limit, and therefore this spectrum must be produced by the return of an originally free electron to an originally ionised atom. The emission of frequency equal to that of the limit of the principal series occurs when an electron with vanishingly small kinetic energy is captured by the positive ion; if the entering electron has a finite kinetic energy, this excess/

excess will be emitted in addition, and as the motion of free electrons appears to be subject to no restrictions such as quantum dynamics imposes on that of the electrons bound in atoms, all values of the kinetic energy will be possible, and the spectrum will be continuous.

Franck [Z.f.Physik,5,428,1921,] and Bajans [Verh. d.deut.Phys.Ges.21,714,1921] have extended this notion to the union of an electron with a neutral electronegative atom. That such a reaction is possible in the case of the halogens is indicated by their general chemical properties, and by the calculations, such as they are, of theoretical physicists on the stability of atoms; J.J.Thomson, for example, finds that a positive charge of 7 units can maintain 8 electrons in equilibrium if they are arranged in three dimensions. [The Electron in Chemistry,p.7]. Franck predicted that the union of an electron with a neutral electronegative atom would give rise to a spectrum, whose long wave limit would correspond to the entrance into the atom of an electron with vanishingly small kinetic energy; the energy in the quantum thus emitted is equal to the difference in energy between the system neutral atom + free electron and the negative ion, and is a measure of the affinity of the atom for an electron. The entrance of an electron with a definite kinetic energy will be accompanied, assuming that none of the energy of/

of the electron appears as additional kinetic energy of the negative ion, by the emission as radiation of energy equal to the electron affinity + the kinetic energy, and the spectrum will, as before, be continuous. When Franck made this prediction, the only halogen which was known to have a continuous band resembling that required was iodine, for which Steubing (loc.cit.) in an investigation of th e visible spectrum had observed the band at 480$\mu\mu$, and Franck suggested that this might be the electron affinity spectrum of iodine.

The matter can be decided only if some independent manner of determining the electron affinity exists; such a method is provided by Born's theory of the crystal lattice [Born;Verh.d.deut.Phys.Ges.21,13,679; Fajans,ibid,pp.539.714]. On the assumption that the ions of the crystal of a salt are maintained in positions of equilibrium under the action of twp forees, (1) the ordinary electrostatic attraction between oppositely charged ions,varying inversely as the square of the distance apart, (2) a repulsive force between oppositely charged ions, varying as the inverse n^{th} power of the distance, where n is a larger number, (10 for alkali halides) which can be calculated from the compressibility of the crystal, Born deduces an expression for U, the energy required to dissociate one gm. mol. of crystal into free gaseous ions;

$$U = \frac{Na}{4\delta}\,\frac{n-2}{n-1} = \frac{Na}{4\delta}\cdot\frac{n-2}{n-1}$$

Where/

where N = Avogadro's Number, $a = 13.95\ e^2$ (e = electronic charge) and δ = the lattice constant. The quantity U may be called the lattice energy.

On the basis of Born's theory, the electron affinity of a halogen atom can be calculated thus:

Starting from positive potassium gaseous ions, and negative chlorine atomic ions, solid potassium chloride can be obtained in two ways.

(I) The two ions may unite to form crystalline salt, whereby an amount of energy U is evolved.

(2) a. The potassium ion may gain an electron, forming a neutral gaseous atom, whereby I_K, the energy required to ionise one gm. atom of potassium vapour, is evolved; I_K can be calculated from the ionisation potential, or, very accurately, from the limit of the principal series of the spectrum.

b. The negative chlorine ion may lose an electron, forming a neutral chlorine atom, whereby an amount of energy E_{Cl} is absorbed, where E_{Cl} is the electron affinity of the chlorine atom.

c. The gaseous potassium may be condensed to solid, whereby L_K, the latent heat of sublimation of potassium (heat of fusion + heat of vaporisation) is evolved.

d. The chlorine atom may enter the molecular form, whereby D_{α}, half the heat of dissociation of I gm. mol. of chlorine gas is evolved.

e. The solid potassium and the molecular chlorine may unite to form crystalline potassium chloride.

whereby/

whereby Q, the heat of formation of I gm. mol. of solid salt from its elements is evolved.

Equating the heat terms in the two processes, we have

$$U = Q + I_K + L_K + D_\alpha - E_\alpha$$

The values of all these factors can be obtained except that of E_{Cl}, which can thus be calculated.

Table II contains the long wave limits of the continuous bands observed, and the corresponding energies in kilogramme calories, and also gives the value of the electron affinities. The latter values are from Landolt-Bornstein, 5th Edt. p. 1585.

Table II.

HALOGEN	1st BAND		2nd BAND		ELECTRON AFFINITY
	λ (μμ)	Energy	λ (μμ)	Energy	
Cl	320	89.1	265	107.5	96
Br	370	77.0	295	96.6	93
I	480	59.3	345	82.3	86
	430	66.3			

It is seen that the second band is associated with an energy agreeing within 5% for Br and I and about 10% for Cl with the calculated values of the electron affinity. Since the data required in the calculation, especially the heats of dissociation of the halogens, are for the most part imperfectly known, the agreement is as close as could be expected. Now the form of these bands is exactly that to be expected in an electron affinity spectrum/

spectrum; so that the position is that the spectrum of each of the halogens, contains a band agreeing in form, and as well in position as the accuracy of the data warrant, with the predicted electrom affinity spectrum, and the most reasonable conclusion is that these bands represent the electron affinity spectrum. Gerlach and Gromann investigated photometrically the two iodine bands at 345 and 480 $\mu\mu$ and, finding that with increasing temperature the intensity of the former band increased while that of the other diminished and was replaced by a line spectrum, concluded that the band of shotter wavelength originated in the atom and the other in the molecule; and they regard the 345 $\mu\mu$ band as the electron affinity spectrum of the iodine atom. On analogy, the 2nd. band of the other two halogens will be the affinity spectrum, and the agreement with the calculated value is maintained in these cases also. Support is lent to the figures indicated by the spectra as the values of the electron affinity by Foote and Mohler's determination of the ionisation potential of hydrogen chloride [J. Amer. Chem. Soc. 42, 1832, 1920.] From the lattice theory, they calculate the ionisation potential of HCl to be 13.7 volts, while the observed value is 14 volts. The electron affinity of chlorine is calculated to be 4.8 volts or 111 Cal., which agrees with the value 107.5 Cal. indicated by the second continuous band.

With repect to the first band, little that is positive can be said. It does not agree with the position to be expected if recombination of neutral atoms were/

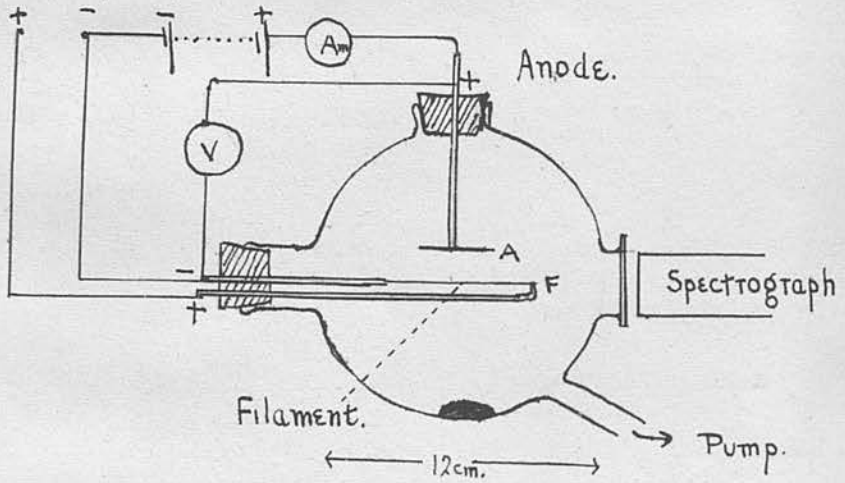
were the cause of the emission; the heats of dissociation of the halogens are about 60 Cal., 46 Cal., and 35 Cal., for chlorine, bromine and iodine respectively. Nor are they due to the reception of an electron by a positive halogen molecular ion, since the ionisation potentials indicate that such emissions would occur far in the ultraviolet, beyond the region examined. Again, the energy evolved in the reaction $X^+ + X^- = X_2$, which appears possible under the conditions of the discharge tube, can be calculated, in the case of iodine, where suficient data are available, and does not approximate to that associated with the first band. To calculate the energy change in this reaction, we proceed thus. An iodine atom may be ionised; the energy required, calculated from the ionisation potential of the atom, 8 volts, is 185 Cal. per gm. atom. The electron removed from the atom may now attach itself to a neutral iodine atom, with the formation of a negative atom ion; 82 Cal., are thus emitted (the electron affinity) The positive and negative atom ions may now unite to form a neutral I_2 molecule evolving the energy x required to be found. The molecule may also be formed directly from neutral atoms, when 34.5 Cal is evolved, and as the same end product has resulted from the same initial substances in both cases, the energy changes must be equal and x can be calculated. x is found to be 137.5 Cal.; the corresponding wavelength/

length is nearly 200 μμ. There seems to be a certain amount of evidence that even a halogen molecule may combine with an electron to form a stable negative molecular ion, and it possible that the first band represents the electron affinity of the halogen molecule; but the data are wanting by which this guess could be substantiated.

Excitation of Halogen Spectra by Electronic Collision.

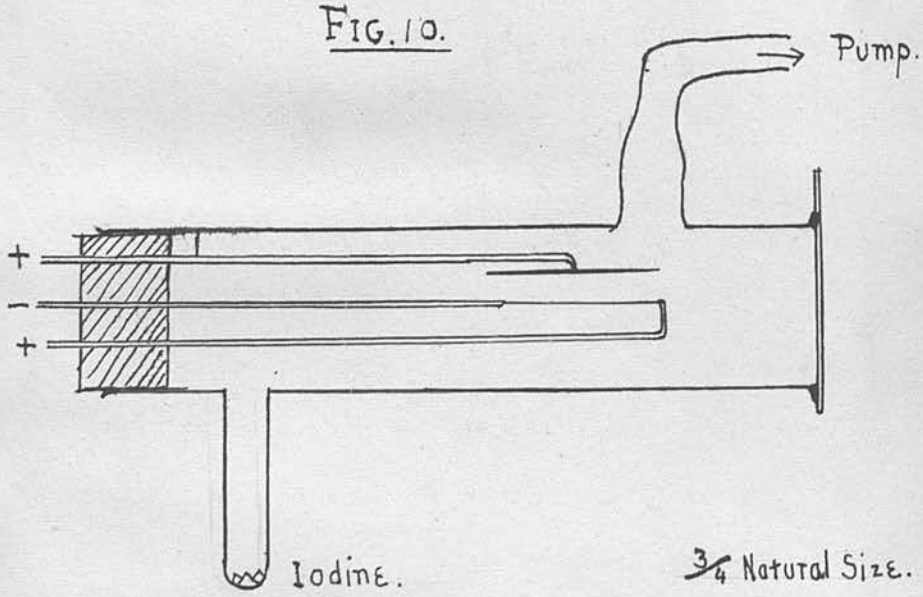
Since an electron affinity spectrum, if it existed might well be a feature of any radiation produced in chemical reaction, it seemed important to endeavour to obtain as direct evidence as possible on the question, and the following experiments were carried out with this object. The spectrum did not show the behaviour anticipated on the assumption that it was an electron affinity emission, but in the experiments the spectrum of iodine was produced by a method which had apparently not previously been applied to an electronegative element. It was expected that if the bands are electron affinity spectra, they should be excited by the collision of the slow moving electrons and even with/

FIG. 9



LOW VOLTAGE MERCURY ARC.

FIG. 10.



3/4 Natural Size.

LOW VOLTAGE IODINE ARC

with electrons possessing vanishingly small velocity with halogen atoms. Moreover, the long wave limit ought to be displaced towards the ultraviolet with increasing velocity of the colliding electron, just as in the X ray region, the limit of the continuous spectrum is displaced towards the short wave region with increasing voltage. The bands were produced by slow electrons, but the other predictions were not fulfilled.

An experiment was first performed in which iodine was contained in an evacuated tube through which was sealed a platinum wire. The wire was raised to a white heat by the passage of a current, and the slit of the spectrograph directed just to the side of the wire. The high temperature would dissociate a considerable number of the iodine molecules in the neighbourhood of the wire, which would be emitting electrons of low velocity, so that the electron affinity spectrum, if it existed, might be expected. No iodine emission was recorded on the plate after half an hour's exposure.

It was then determined to repeat the experiment with accelerated electrons by the method introduced by Franck and Hertz and used in the elucidation of the spectra of metallic vapours and of the inert gases. Electrons are emitted by a heated filament and are accelerated towards an anode at a definite voltage with respect to the filament. The anodic voltage required to cause the appearance of the various features of the spectrum/

spectrum can be determined, and the energy possessed by the colliding electron as the result of the fall through the potential difference between filament and anode compared with the energy in the quantum emitted by the gas.

A trial was first made with mercury, in the apparatus shown in fig. 9 . The tungsten filament F was brought to a white heat by the passage of 4 to 5 amps. from the 100 volt direct current circuit. The anode A was a platinum ~~ship~~ strip 2 cm × 1cm; the anodic voltage was applied from a "high tension" battery such as is used in wireless, whose negative pole was connected to the negative end of the filament. A milleammeter was included in the anode circuit, and a voltmeter connected between the anode and the negative end of the filament. A globule of mercury was placed in the bulb, the apparatus evacuated to 0.004 mm., and the mercury gently warmed by the hot gases from a small bunsen flame. The spectrum of the region between the filament and anode was photographed through a quartz window. In the experiment, the anode was at 30 volts with respect to the negative end of the filament, and a very rich arc spectrum of mercury was produced with 8 minutes exposure. (Fig, 11.). With mercury, ~~the~~ electron currents of 0.1 amp. could readily be obtained.

The form of apparatus used with iodine, fig 10. was substantially the same. The filament was of tungsten wire/

wire, and the anode of platinum foil 2.5 cm. × I cm.; the supporting leads were iron. The experiments were performed with iodine vapour at 0.I3 mm. It was soon found that it was much more difficult to pass a current between the filament and anode in the presence of iodine than it was for mercury; while, for mercury electron currents of 0.I amp. passed, the greatest current observed in the presence of iodine was IO^{-4} amps. This was for an anodic potential of 60 volts; for lower potentials the electron current was much smaller, and was indicated only by a sensitive moving coil galvometer, one division of which corresponded to IO^{-7} amps.* In the presence of iodine the filament rapidly disintergrated, and had to be ~~repaleed~~ replaced after about an hour.

Fig.12 shows the results obtained.

(a) I hours exposure for an anodic potential of 60 volts, is identical with the spectra obtained by the Tesla discharge. The two sets of band spectra appear, along with the sharp line at 206.I $\mu\mu$. The general continuous ground of the second band spectrum is weaker than that obtained in the Tesla spectrum, and the bands across it are comparatively more prominent, as with small currents in the Tesla discharge.

(b) I hour's exposure at 5I volts is identical with (a).

(c) I hour's exposure at 36 volts; position of bands identical with those in(a) and (b).

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of the head of the band at 345 $\mu\mu$, and a very faint trace of the line at 206.I $\mu\mu$.

The results show, first that it is very difficult to produce the bands at anodic potentials of I2 volts; and secondly, that the position of themaximum is independant of the voltage, facts that are difficult to explain on the simple theory of electron affinity spectra. Since performing the experiments, however, I have found that Stark [Ann.d.Physik.52,259, I917] who investigated the continuous spectrum of hydrogen beginning at the limit of the Balmer series, likewise was unable to notice any displacement of the maximum with increasing velocity of the positive rays by which the hydrogen was bombarded. The form of this band is identical with that of the continuous bands observed in the halogen, and as there is no doubt that the theory of the hydrogen band accounts for the position and character, apart from the distribution of intensity, in a very satisfactory manner, the results of t he experiments on the action of the slow electrons on the halogens cannot be said to invalidate the conception that the halogen bands originate in the process anologous to that giving rise to the hydrogen band, and represent the electron affinity spectrum. In fact, it appears that all questions of intensity dsitribution in continuous spectra both in the X ray and in the ultraviolet and visible regions have so far resisted all attempts at a theoratical explanation. [See Sommerfeld, Atomic Structure and Spectral Lines (English Trans) pp.I79,45I.]

THE IONISATION OF IODINE VAPOUR BY ULTRA VIOLET LIGHT:

The investigation of the action of short wave length ultraviolet light on iodine vapour was suggested by the discovery of the iodine line series beginning at 206$\mu\mu$.

There is a close similarity between the effect of radiation and of electron impact on atoms. The valency electron of the sodium atom can be raised from its normal orbit, 1s, to the next orbit, 2p, either on collision with an electron whose kinetic energy is equal to the energy required to effect the change, or by the absorption of radiation whose quantum is just sufficient. Similarly, ionisation cen be effected by an electron whose kinetic energy is sufficient to raise the valency electron from the nromal orbit to a position where it is beyond the influence of the positive residue, the necessary energy being equal to the quantum emitted when a free electron returns to the positive ion with the emission of the limiting wavelength of the principal series. Conversely, it is be expected that exposure of the vapour to radiation of wavelength equal to or shorter than that of the series limit will cause ionisation of the ~~other~~ atom.*

* NOTE. For ionisation ,but not for resonance, a quantum of radiation greater than that required to cause the change will be effective; to produce resonance,i.e. the raising of an electron from one stationary state to another within the atom, the quantum must be exactly equal to the energy difference between the two states. In the former case, any surplus energy of the quantum can go to increase the kinetic energy of the emitted electron, while, since it appears to be impossible to increase the kinetic energy of an atom by directly by the absorption of radiation, there is no corresponding reservoir for surplus energy in the production of resonance.

Ionisation of air and of other gases by short wavelength ultraviolet light has been observed [Lenard & Ramsauer; Sitz.d.Heidelberg.Akad.d.Wiss. I IO-II; J.J.Thomson, Proc. Camb. Phil. Soc. XIV, 417, (1907); Hughes ibid, XV, 483 (1910)] while more recently the equivalence of the minimum quantum of radiation required to cause ionisation to the energy emitted when a free electron falls into a positive ion seems to have been indicated by the observation that light of wavelength shorter than the limit of the principal series can cause ionisation of caesium vapour, light of longer wavelength being quite ineffective, [Williams & Kunz. Phys.Rev. I5,550 (1920).]

None of the halogens had been caused to lose electrons under the influence of light. [Ludlam [Phil.Mag. [VI], 23, 757, (1912)] showed that no ionisation was produced in chlorine by any of the ultraviolet light which passes through fluorite, the substance most transparent to these radiations. The ionisation of iodine vapour by light had been searched for with negative results by several investigators. [Henry, Proc. Camb. Phil Soc. IX, 319, (1898); Whiddington, ibid, XV, 189, (1910).] These workers, however, used arrangements in which the light had to pass through quartz and glass, and considerable lengths of air, so there could have been no very short wavelength ultraviolet radiation acting on the iodine. A consideration of the ultraviolet line spectrum of iodine shows that the light used by these investigators was of too low frequency. The ionisation potnetial of the iodine/

iodine atom has been found to be 8 volts; [Smythe and Compton, Phys.Rev. I6,501,1920]; the corresponding wavelength, 150 $\mu\mu$, will be the limit of a line series; and that a series did exist in this region was shown by the discovery of the line at 206 $\mu\mu$ and those of shorter wavelength. Ionisation of the iodine atom is therefore to be expected by light of wavelength shorter than 150 $\mu\mu$. It would, however, be exceedingly difficult to test the ionisation of iodine by light at temperatures high enough to cause any considerable dissociation to atoms, owing to the spurious effects of thermal ionisation of the metallic parts of the apparatus, and especially since iodine vapour itself has been found to conduct at high temperatures; but ionisation of the molecule might take place if the energy of the quantum were sufficient first to cause dissociation to atoms, and then to ionise one atom. The energy of dissociation of iodine molecules corresponds to I.4 volts, so that the ionisation potential of the molecule would be 8 + I.49 = 9.5 volts. Actually, an ionisation potential has been found in iodine vapour at this value. [Smythe and Compton, Phys. Rev. I6, 501, 1920, give 9.4 v; Mohler and Foote, ibid, I5, 321, (1920) give I0.IV] The corresponding wavelength is I30 $\mu\mu$, which is in the region transmitted by fluorite, and it was determined to search for conductivity in iodine vapour exposed to light of the fluorite-ultraviolet.

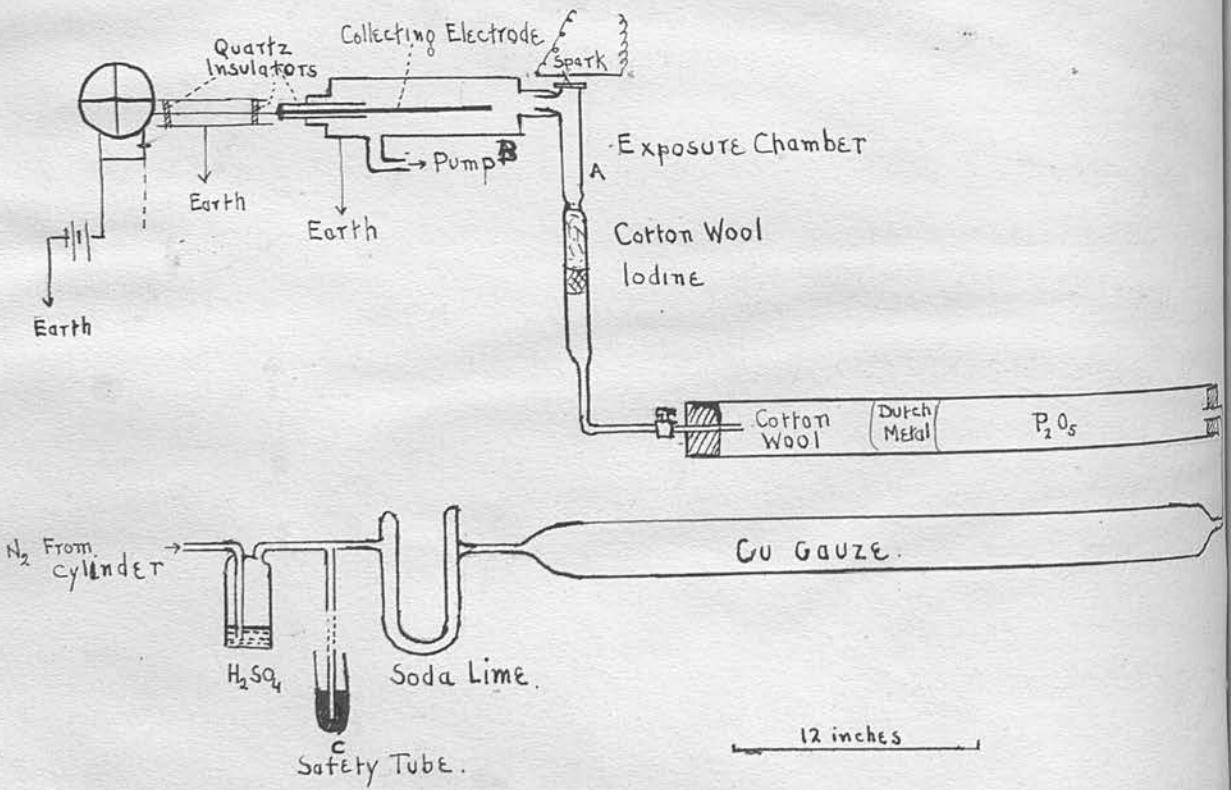
EXPERIMENTAL/

EXPERIMENTAL: As the source of light, a powerful spark between aluminium terminals one cm. apart was used. That the radiation from this source would probably be effective in producing ionisation was indicated by Lenard's success in ionising air and other gases by the light from the aluminium spark; also Lyman's photograph of this spark in air shows groups of strong lines at 176 and 130 $\mu\mu$, in the region expected to be effective. [Lyman, Spectroscopy of the Extreme Ultraviolet, frontispiece.] The spark, contained in an earthed metal box to prevent possible electrical disturbances of the electrometer, was driven by a 10,000 volt transformer taking a primary current of 10 amps. at 230 volts. In parallel with the spark gap was a condenser of capacity 0.006mF. The spark gap was placed practically touching the fluorite window of the exposure chamber, so that, during the discharge, the glowing vapours played against the window, which had therefore to be cleaned frequently, and eventually became so pitted as to lose much of its transparency. It was found that the close proximity of the spark to the window was a necessary condition for the production of the effect to be described.

The great difficulty to be overcome in experiments to test for ionisation in gases is the spurious effect caused by the photoelectric emission of electrons from/

FIG. 13.

IONISATION OF IODINE VAPOUR.



from the electrodes under the influence of the ionising radiation. All metals exhibit a pronounced photo - electric effect on exposure to radiation of much lower frequency than that anticipated to be required for iodine. Since, however, only negative charges are given off by metals exposed to light, the arrival of positive charges at a suitable collecting electrode will be a criterion for the existance of ionisation within the volume of a gas.

The first experiments were made in a glass apparatus to which the window was cemented, but the lar ge currents due to the photoelectric effect at the platinum electrodes caused the method to be abandoned in favour of one in which exposure to the light could be made in a chamber apart from the vessel in which the ions were detected.

The exposure chamber A, (fig.I3) consisted of a glass tube ½ cm. in diameter, on the end of which was cemented a clear colourless fluorite window I.3 mm. thick. A shorter side tube led to the copper ionisation chamber B, the outer cylinder of which was earthed. The collecting electrode, of copper wire, insulated from the earthed cylinder by quartz, was connected to one pair of quadrants of a Dolezalek electrometer, the connecting wire, en closed throughout in an earthed metal tube, being about a metre long in order to remove the electrometer from the neighbourhood of the spark. A side tube from the ionisation chamber led to a rotatory oil pump/

pump . The electrometer, contained in an earthed metal box, was arranged so that a potential difference of one volt between the quadrants gave a deflection of 200 mm. on a scale at a distance of I metre from the mirror. Although greater sensitivity could have been attained by the use of finer suspensions for the needle, and by charging the needle to a higher potential than the 72 volts used, the arrangement described above proved in practice the most convenient. The needle was charged by two "high tension" batteries as used in "wireless" permanently connected to it. The two sets of quadrants could be joined by means of a key, worked by a string of unspun silk from a position near the scale.

In the experiments with iodine, solid iodine was placed in the exposure tube, and a stream of nitrogen at low pressures (I - IO mm.) passed over in order to carry a current of iodine vapour past the window. The solid iodine was protected fr om the action of the light by a tightly packed plug of cotton wool, which also served to retain any particles of dust.

The nitrogen was obtained from a cylinder of the compressed gas; it was passed through concentrated sulphuric acid, over soda lime, over a long length of tightly rolled copper gauze at a bright red heat (previously well heated to remove grease, and heated in hydrogen before each group of experiments) to remove oxygen, dried by passing through a long tube of phosphorus/

phosphorus pentoxide, passed over Dutch metal foil to remove any mercury vapour (from the safety tube C) and finally passed through a long length of tightly packed cotton wool to remove dust. This latter precaution is an important one, since any photoelectric ionisation of dust particles might give rise to positively charged particles which could reach the collecting electrode.

Nitrogen was chosen to maintain the stream, as it seemed likely not to be ionised by the light employed. Nitrogen scarcely absorbs in the fluorite ultraviolet and it is difficultto see how ionisation can be produced without absorbtion.

Experiments with Pure Nitrogen: These were carried out to ascertain if ionisation of nitrogen was produced by the light transmitted by fluorite. The Method of experiment was this. A potential was applied to the quadrants and the collecting electrode; the quadrants were then separated. If the insulation had been perfect, separation of the quadrants would have caused no deflection; but actually the needle slowly crept across the scale as the result of slight leaks in the insulation. The pump was started; the number of scale divisions passed by the painter in a minute immediatley preceeding the exposure determined; five seconds exposure to the light given, and the number of divisions passed over in the minute beginning with the commencement/

commencement of the exposure determined; the leak in the next minute without exposure measured; a fresh exposure given and theleak noted, and so on.

The following are some of the results obtainedin such blank experiments.

TABLE III - EXPERIMENTS WITH NITROGEN

Pressure of Nitrogen I mm.

Potential on Collecting Electrode - 4v.			Potential on Collecting Electrode + 4 volts		
Minute	+Leak without Expos.	+Leak with Expos.	Minute	-Leak without Expos.	-Leak with Expos.
4th	6		3rd	I2	
5		6	4		I0
6	6		5	I0	
7		7	6		II
8	6		7	I0	
9		6	8		8
I0	6		9	I0	
II		6	I0		7
I2	6		II	8	
I3		6	I2		I0
I4	5		I3	6	
I5		5	I4		I0
I6	5		I5	6	

TABLE IV - EXPERIMENTS WITH NITROGEN

Pressure of Nitrogen 4 mm.

Potential on Collecting Electrode - 3volts			Potential on Collecting Electrode +3volts.		
Minute	+leak without Expos.	+Leak with Expos.	Minute	-leak without Expos.	-Leak with Expos.
3rd	I4		2nd	I0	
4		I4	3		I0
5	I2		4	9	
6		I0	5		9
7	II		6	7	
8		II	7		9
9	8		8	8	
I0	8		9		6
II		8	I0	9	
I2	9		II		9
I3		8	I2	4	
I4	6		I3		6
I5		6	I4	5	
I6	6				

There/

There is no greater positive leak for illuminated than for non-illuminated nitrogen; also, since the negative leak with exposure is sacrcely any greater than that without, it is evident that exposure does not cause the collecting electrode to receive any considerable number of electrons, so that photoelect ric emission of elect rons from the metal parts is, at most, slight.

EXPERIMENTS WITH IODINE VAPOUR: Iodine was now placed in the tube, and the experiments repeated, all other arrangements being exactly as before. (Table V)

TABLE V NITROGEN + IODINE

Pressure of Nitrogen 2mm, Pressure of Iodine, 0.I8mm.

Potential on Collecting Electrode: -4v			Potential on Collecting Electrode: +4 v.		
Minute	+leak without Expos.	+leak with Expos.	Minute	-leak without Expos.	-leak with Expos.
2nd	I4		2nd	I2	
3		32	3		33
4	I6		4	I3	
5		26	5		24
6	II		6	I3	
7		27	7		26
8	I2		8	I0	
9		25	9		22
I0	8		I0	I0	
II		25	II		26
I2	8		I2	9	
2nd	I0		2nd	24	
3		26	3		48
4	9		4	I9	
5		32	5		36
			6	20	
			7		25

Several experiments confirmed these results; they show that there is a decided increase in the leaks on exp-

osure/

exposure. When charged in the appropriate manner, the collecting electrode can receive either positive or negative charges when iodine vapour is exposed to light. For any set of observations the difference between the leak in a minute containing a 5 second's exposure and the leak per minute without exposure is approximately constant; assuming the capacity of the electrometer to be about 50 e.s.u. (the order of the value for these instruments; see Crowther, "Ions, Electrons, and Ionising Radiations", p.I2) the ionisation current produced by the light can be calculated from the equation $S = C\frac{dV}{dt}$, where S is the current, C the capacity of the electrometer, and $\frac{dV}{dt}$ the rate of change of potential between the quadrants. This equation takes the form $S = \frac{C d}{300 D}$ where C is the capacity of the system in electrostatic units, d is the number of divisions passed over by the spot of light per second, and D the deflection caused by a potential difference of one volt between the quadrants; the current S is in electrostatic units. From Table V, the average increase in the deflection due to positive charges reaching the collecting electrode on exposure is I5 divisions for 5 seconds exposure; d therefore is $\frac{15}{5} = 3$; D = 200, whence $S = 2.5 \times I0^{-3}$ e.s.u. $= 8 \times I0^{-13}$ amps. In most of the experiments the negative leak was slightly greater than the positive; this may be due to the slight surface ionisation, but evidently such an effect is but small.

Some/

Some experiments were performed with the pump out of ac tion; in this case illumination caused no increase in the positive charge assumed by the collecting electrode; recombination of the ions apparently took place before they reached the electric field. As Table VI shows, exposure appeared to cause a slight but real increase in thenumber of negative charges reaching the collecting elctrode, even when thepump was not in action. This may be due to slight photoelectric ionisation of the metallic parts; but there is also the possibility of the emission of radiation in the process of recombination of an electron and a

TABLE VI.

Potential on Collecting Electrode, + 4volts.

Pump not running			Pump running		
Minute	-leak without Expos.	-leak with Expos.	Minute	-leak without Expos.	-leak with Expos.
2nd	II		I4th	8	
3		I3	I5		I8
4	I0		I6	7	
5		I2	I7		I4
6	8		I8	8	
7		I0	I9		I4
8	8		20	8	
9		I4	21		I6
I0	8		22	7	
II		I0			
I2	I0				
I3		9			

positive iodine ion, which would cause a photoelectric effect at the electrode. Table VI records a continuous series of observations of the negative leak; for the first I3 minutes the pump was out of action; at

the/

the 14th minute it was started. Exposure causes only a slight increase in the number of negative ions reaching the electrode when the pump is not running, but the operation of the pump immediately causes a considerable increase in the negative leak on exposure. After a number of experiments had been performed, results were obtained which apparently contradicted the earlier ones; exposure caused no increase in conductivity. It was finally noticed that the aluminium sparking terminals had become covered with a layer of oxide. The spark between terminals in this condition is feeble in ultraviolet radiation; for instance, it was found that a screen coated with barium platinocyanide placed in the spectrograph fluoresced with much diminished intensity in the portions exposed to short wavelength ultraviolet light from a spark between oxide-coated terminals. When the terminals were cleaned the ionisation in iodine vapour was again strongly produced. This appears to be additional evidence that the effect is not due to spurious electrical disturbances from the spark, since these would be as likely to originate from a discharge feeble in ultraviolet light as from one rich in this radiation.

Upper Limit of the Effective Wavelength: It is at present impossible to determine accurately the limiting wavelengths associated with phenomena in the ultraviolet region beyond 200 $\mu\mu$, at least without the use of a vacuum spectrograph with fluorite optical parts to act as monochromator. Fluorite, quartz and the oxide/

oxide of boron are theonly solids transparent in this region, boric oxide and quartz do not transmit light beyond about I60$\mu\mu$. With respect to the possibility of forming a graduated series of gaseous filters, sufficient data on the absorption of gases in this region do not exist t o lead to any conclusion. Oxygen, however, is known to possess a very strong absorption band, rising very rapidly beyond I85$\mu\mu$ and extending throughout the region transmitted by fluorite. Experiments were therefore performed to determine if the radiation effective in ionising iodine vapour was strongly absorbed by oxygen. The spark was removed I cm. from the window and the usual readings of leak made.

Tables VII to IX. give the result.

Table VII records the results normally obtained with the spark touching thewindow; table VIII gives the readings observed immediately after those shown in table VII with the spark I cm. from the window; and table IX those observed immediately after making the readings recorded in table VIII, with the spark replaced close to the window.

TABLE VII Spark touching window.

Potential of collecting Electrodes -4 volts.

Minute	+leak without Expos.	+leak with Expos.	Minute	+leak without Expos.	+leak with Expos.
2nd	I0		9th		20
3		2I	I0	7	
4	II		II		I6
5		I5	I2	7	
6	8		I3		2I
7		28	I4	8	
8	7		I5		I3
			I6	6	

TABLE VIII Spark I cm from Window.

Potential of Collecting Electrodes -4 volts.

Minute	+leak without Expos.	+leak with Expos.	Minute	+leak without Expos.	+leak with Expos.
1st	I4		9th	I4	
2		I4	I0		I2
3	I6		II	I3	
4		I8	I2		I2
5	20		I3	I2	
6		I6	I4		II
7	I4		I5	II	
8		II			

TABLE IX Spark touching window.

Potential of Collecting Electrodes -4 volts.

Minute	+leak without Expos.	+leak with Expos.	Minute	+leak without Expos.	+leak with Expos.
2nd	I4		8th	I2	
3		32	9		25
4	I6		I0	8	
5		26	II		25
6	II		I2	8	
7		27			

These experiments show that removal of the spark I cm. from the window causes the effect to cease, while trials made immediately before and after, with the spark touching thewindow, other conditions being the same, show a strong effect. The suppression of ionisation on removal of the spark must be due to the absorption of oxygen, whereby it is indicated that the wavelength of the effective radiation is shorter than I85 $\mu\mu$.

Finally, af ter the series of experiments with iodine, the apparatus was cleaned, and the experiments with pure nitrogen repeated, and the results comfirmed.

Summary/

Summary of results:

(1) Nitrogen flowing through the apparatus at pressures of 1 to 10 mm. showed no conductivity on illumation by the light of the aluminium spark transmitted by fluorite.

(2) When the nitrogen stream contained iodine vapour of pressure 0.18 mm., exposure to the light required a current of the order 10^{-13} amp.

(3) Both positive and negative ions were given to the electrometer in nearly equal amounts, the negative being in slight excess.

(4) The effect was not observed in the absence of a stream of vapour.

(5) The effect ceased when any kind of film formed on the fluorite, or when the light source was removed 1 cm. from clean fluorite.

(6) A well working spark was necessary to produce the effect.

Discussion of Results. The absence of conductivity on illumination of pure nitrogen shows that the effect produced by light in the presence of iodine vapour is not a surface ionisation, since at least as much light would reach the metal parts in the first case as in the second. Nor does the effect appear to be due to electrical disturbances caused by the proximity of the spark, as these also would have appeared with nitrogen.

The/

The only difference between the experiments with nitrogen, in which illumination caused no current, and those in which an easily detectable current was observed on illumination, was the presence of iodine, and the current is therefore to be attributed to the ionisation of gaseous iodine, by ultraviolet light. The effective light is of shorter wavelength than that of the red limit of the oxygen absorption band at about 185$\mu\mu$ and must be of longer wavelength than about 100$\mu\mu$, where fluorite absorbs, unless indeed the very penetrating radiation from the aluminium spark reported by Lenard [Sitz.Heidelberg.Akad.d.Wiss. p.31, 1910] to which he ascribed a wavelength beyond the spectroscopically undetermined absorption limit of fluorute is partly effective. The evidence for such a radiation, however, does not appear very definite.

The observations of critical potentials in iodine vapour lead to the expectation that ionisation of the molecule should occur on exposure to wavelength 130$\mu\mu$, and of the atom to 150$\mu\mu$. There is a strong group of aluminium lines about 130$\mu\mu$, so that the light used would be effective for either of these processes. As the experiments were carried out at ordinary temperature, there would be primarily very few iodine atoms, though the possibility of the dissociation of the molecule by light is not excluded. Most of the ionisation must be due to molecules.

It is, however, probable that light of longer wavelength/

wavelength than 130 $\mu\mu$ will be able to ionise iodine molecules. Iodine fluoresces under the influence of visible and ultraviolet light; the molecule absorbs a quantum of radiation, thereby assuming a state of greater energy, the return from which to the normal st state liberates the energy of excitation as fluorescent light. Such an active molecule may be regarded as "partly ionised", and will require less energy to raise it to the state of complete ionisation than the normal molecule. This has already been proved for electron impact by Smythe and Compton (loc.cit.) who found that the ionisation potential of fluorescing iodine molecules was less than that of normal molecules by an amount equivalent to the energy in the quantum exciting the fluorescence. It has also been observed that for the some potential difference between the electrodes of a tube containing iodine vapour, the current in the glow discharge is greater for the fluorescing than for the normal vapour. [Franck and Westphal; Verh.d.deut. Phys.Ges. 14, 159 (1912).] In thesame way it might be expected that iodine vapour exposed to light containing a wide range of wavelengths could take place in two stages; first the activation to the state of fluorescence and then the ionisation of the fluorescing molecule, the energy required in the second step being less than that required to ionise the normal molecule by the energy into the quantum necessary to cause fluorescence The wavelength corresponding to the observed ionisation potential/

potential of fluorescing iodine, 6.8 volts, is 180$\mu\mu$, which is well within the range of the radiation available in these experiments, but which would have been absorbed before reaching the iodine in the apparatus used by previous investigators.

The general conclusion is that the conductivity observed in these experiments was due to the ionisation of iodine molecules by light of wavelength shorter than 185$\mu\mu$, and it seems probable that the fluorescing molecules contributed a share.

The main interest to chemists of these results on the ionisation of gases by light is that they indicate the value of the energy of ionisation, an important quantity in modern chemical theory. Only on the basis of precise knowledge of this quantity can hypotheses of values be constructed with respect to the elementary electronic mechanism of chemical change. For example, a plausible enough explanation of the course of photochemical reactions such as the union of chlorine and hydrogen, can be formulated on the supposition that the photoionisation of the gas is the initial stage. [Bodenstein, Z. phys. Chem. 85, 333, (1913)] The experiments of Ludlam on the action of ultraviolet light on chlorine showed that the explanation was untenable; and in general it may be stated that the frequencies required to ionise gases are so great that complete photoionisation cannot be a preliminary in any/

any photochemical reaction between gases which takes place in visible or ultraviolet light of wavelength longer than those of the Schumann region. On the other hand, activation of the reactants in the sense that an electron is displaced from its normal orbit to one of greater energy is a possible initial st age in photochemical reactions, and may very well be the primary reaction.

Emission Spectra of the Halogen Hydrides:

The formation of the halogen hydrides seemed a reaction in which the emission of chemical radiation, if it exists, is likely. One stage will be transference of the electron of the hydrogen atom to the chlorine atom, a process which may be accomapnied by the emission of radiation. In the passage of an electric discharge through the hydrogen halides at low pressure decomposition of the gases occurs; since the decomposition is produced by electron impact, or by collision with charged ions, or by the radiation emitted in the passage of the current, it will probably be a monomolecular dissociation into hydrogen and chlorine atoms; the reunion of these is the reaction which it was hoped to study. The spectra of the halogen hydrides were therefore examined with the object of ascertaining if any emission were present which could be interpreted as due to the union of hydrogen and the halogen.

An indication, of the position in which such radiation is to be expected is afforded by the heat of formation of the hydrides from their constituent atoms. These can be calculated thus:

(See next page)

$H_{2\,gas} = 2H_{gas} - 84\,Cal$ [Landolt-Bornstein, 5th Edn. p. 1585]

$Cl_{2\,gas} = 2Cl_{gas} - 55\,Cal$ [Henglein, Z. f. anorg. Ch. 123, 137, (1922)]

$2H_{gas} + 2Cl_{gas} = 2HCl_{gas} + 2x$

also, $H_{2\,gas} + Cl_{2\,gas} = 2HCl_{gas} + 44\,Cal$ [L.B. 5th Ed. p 1489]

$\therefore 44 = 2x - 84 - 55$

$x = 92\,Cal.$

For HBr,

$H_2 = 2H_{gas} - 84\,Cal$

$Br_{2\,liquid} = Br_{2\,gas} - 7\,Cal$ [L.B. 5th Edn. p 1445]

$Br_{2\,gas} = 2Br - 46\,Cal$ [Bodenstein, Z. f Elektroch. 22, 31, (1916)]

$2H_{gas} + 2Br_{gas} = 2HBr_{gas} + 2x$

also, $H_{2\,gas} + Br_{2\,liquid} = 2HBr_{gas} + 16{\cdot}8\,Cal$ [L.B. p 1489]

$\therefore 16{\cdot}8 = 2x - 46 - 7 - 84$

$x = 77\,Cal.$

For HI,

$H_2 = 2H_{gas} - 84\,Cal$

$I_{2\,gas} = 2I_{gas} - 34{\cdot}5\,Cal$ [Starck + Bodenstein, Z. f. Elektroch, 16, 966, 1910]

$2H_{gas} + 2I_{gas} = 2HI_{gas} + 2x$

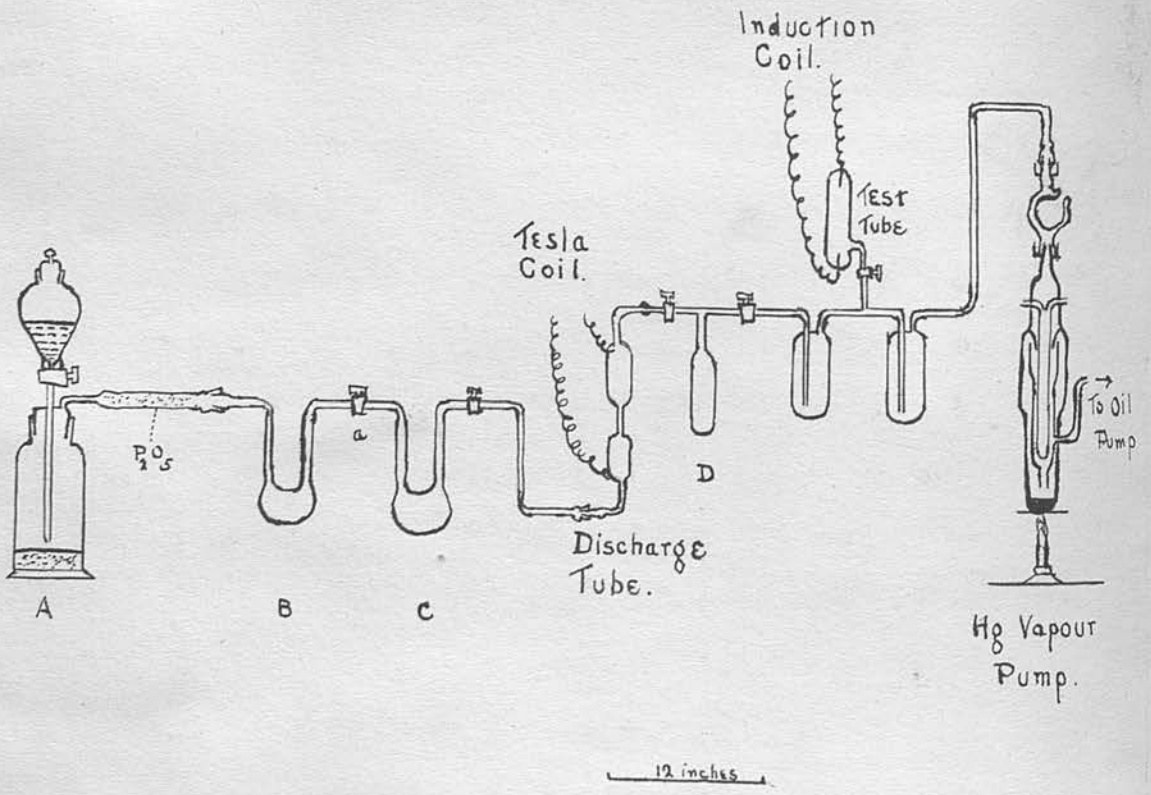
also $H_{2\,gas} + I_{2\,gas} = 2HI_{gas} + 2{\cdot}9\,Cal$ [L.B. p 1489]

$2{\cdot}9 = 2x - 34{\cdot}5 - 84$

$x = 61\,Cal$

FIG. 14.

ARRANGEMENT FOR SPECTRA OF HCl, etc.



To face p 64.

The corresponding wavelengths are

for HCl, 309 μμ.

for HBr 340 μμ.

for HI 466 μμ.

Procedure. Trouble was again experienced in obtaining pure spectra, and the method finally adopted was to photograph the spectrum during the passage of a continuous current of gas through the tube.

Hydrogen Chloride: The apparatus was fitted together as shown in fig. 14 , joints being made by grinding, or at the blow-pipe. The pumping system consisted of a mercury condensation pump, backed by a rotatory oil pump; the necessary traps were introduced to prevent access of mercury vapour to the halogen or vice versa. Pure sodium chloride was placed in A, and the apparatus evacuated by the oil pump while being heated with the naked flame. The bulb B having been immersed in liquid air, concentrated sulphuric acid was dropped on the salt in A. The HCl, freed from most of any moisture by its passage through phosphorus pentoxide, condensed in B as a snow white solid. Two thirds of the contents of B were slowly distilled into bulb C, immersed in liquid air, the temperature of B being maintained throughout below the melting point of hydrogen chloride, The residue in B, containing any non volatile impurities was rejected. The apparatus was now thoroughly evacuated up to tap "a" by the diffusion pump;/

pump; and the temperatures of the bulbs C and D were now arranged so that a stream of the gas passed through the discharge tube at a convenient pressure. The spectra were excited as before.

Hydrogen Bromide: The apparatus was evacuated by the oil pump and hydrobromic acid solution, of specific gravity I.49 dropped very slowly on phosphorus pentoxide placed in A. The reaction was carried out so slowly that little rise in temperature took place, which might have caused the decomposition of the HBr by phosphoric acid. No evidence of the formation of bromine was observed. The gas was passed over phosphorus pentoxide and a little red phosphorus, and condensed in B, from which it was ~~practically~~ fractionally distilled.

In the passage of the current, the gas was decomposed and complete recombination did not take place. Solid bromine collected in bulb D, while hydrogen remained uncondensed; on breaking connection with the ~~p~~ pump, the pressure of hydrogen rose, and in the end, its spectrum masked that of the bromine. In the experiments, connection to the pump was maintained throughout.

Hydrogen Iodide: was similarly prepared by dropping concentrated hydriodic acid solution, freshly distilled over red phosphorus, on phosphorus pentoxide, and was fractionally distilled as before. The passage of the discharge again caused decomposition.

Results: The spectra appear to be identical with those/

those of the corresponding halogens with the addition of the first members of the Balmer series of hydrogen (Fig. I5)The band spectra disappear at very low pressures. At pressures above 0.0I mm. the second continuous band is the most prominent feature in the spectra. For hydrogen iodide, the sharp line spectrum found to be characteristic of iodine is again prominent. There is no feature in the spectra of the hydrides additional to those in the emissions of their constituent atoms which can be attributed to chemical radiation originating in the union of the neutral atoms. It is possible that under the conditions of the discharge no reaction occurs between neutral atoms but rather between negative halogen ions and hydrogen nuclei. Measurments of the ionisation potnetial of hydrogen chloride lead to the conclusion that the effect of a collision between an electron with a HCl molecule is to cause the disruption of the connection between the hydrogen and chlorine ions; $H^+ - Cl^-$ $H^+ + Cl^-$. In the reverse reaction, an amount of energy equivalent to the kinetic energy of an electron which has fallen through I4 volts (the ionisation potential observed by Foote and Mohler J.Am.Ch.Soc. 42,I832,I920) will be given out, and if this is emitted as one quantum, the spectrum will contain a band at the corresponding wavelength 88$\mu\mu$, far beyond the region examined.

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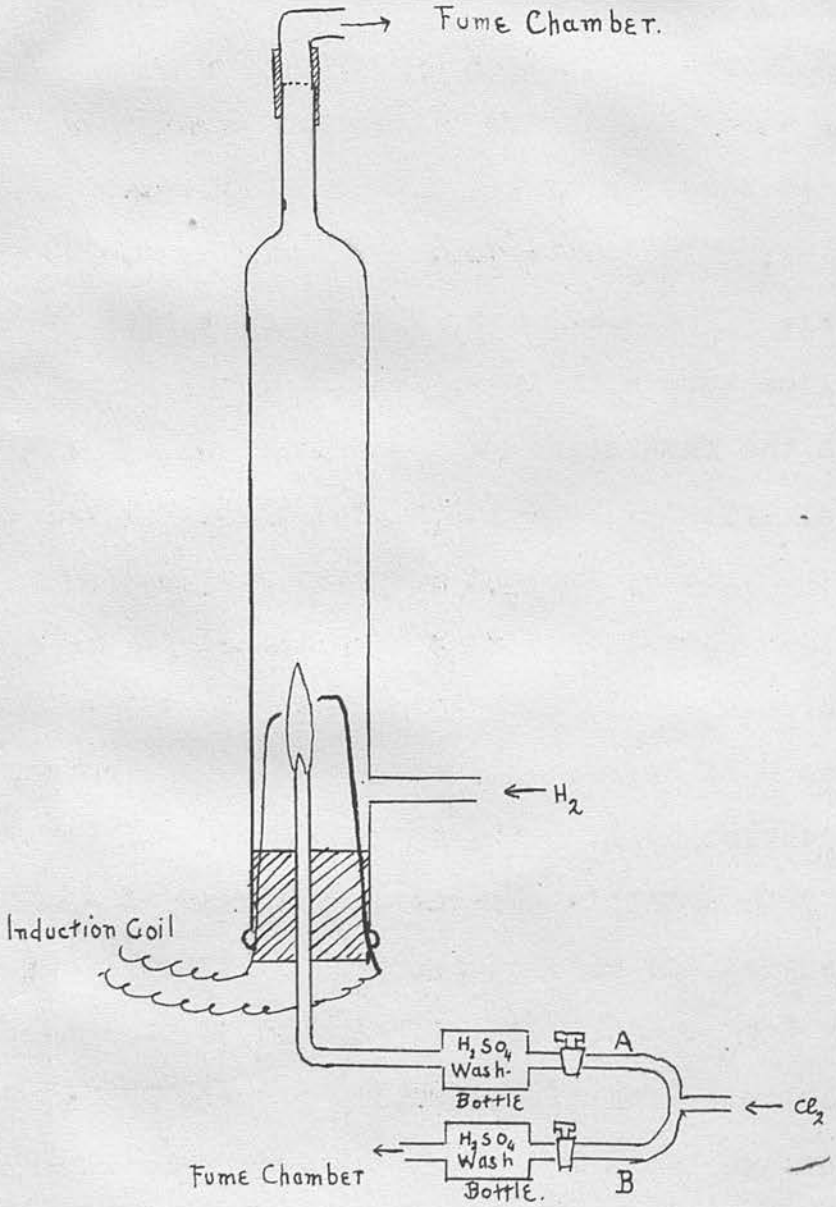
FIG. 16

HYDROGEN- CHLORINE FLAME.



Natural Size.

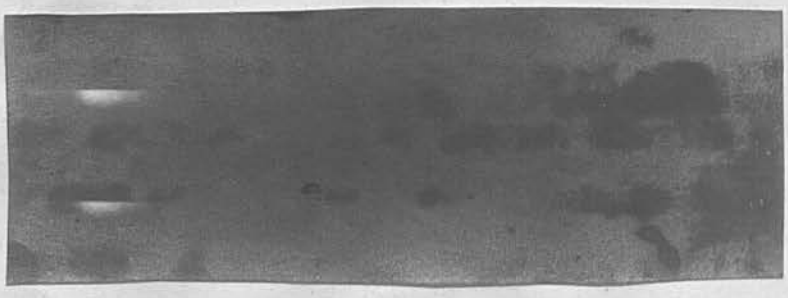


FIG. 17.

Spectrum of the H-Cl Flame.

Study of Some Specific Chemical Reactions:

(I) The Union of Hydrogen and Chlorine. Since no reference was found in the literature concerning the ultraviolet spectrum of the flam e of hydrogen burning in chlorine, experiments were performed to investigate the matter. The apparatus (fig.16) consisted of a clear silica tube with inlet tubes for the gases, and outlet to the fume chamber. The chlorine, from a commercial cylinder, was introduced through a narrow quartz tube fitting through a rubber stopper, while the hydrogen passed through a tube sealed to the quartz. For thepurpose of kindling the flame, two silver electrodes were introduced, connected to the secondary of an induction coil. The apparatus was filled with hydrogen from a Kipp's generator, a stream of sparks passed between the electrodes, and thechlorine was carefully introduced. The first rush of chlorine from the cylinder, which had rather a stiff valve, was passed through the arm B of the Y piece; the current was then regulated, and connection made to the flame chamber. Irregularities of flow produced by the bubbling in the wash bottle were avoided by the introduction of a capillary tube in front of the flame chamber.

The flame, consisting of a bright core surrounded by a more diffuse region, had a livid white colour; exposures of 45 minutes were required to form an impression on the plates. The resulting spectrum, shown in fig.17 was quite continuous. It starts strongly in the red (probably extending to the infra red/

red), and extends throughout the visible and ultraviolet regions to beyond 300 $\mu\mu$. The apparent minimum of intensity in the green is due to the comparative nonsensitiveness of the panchromatic plate in this region. Observed visually, the spectrum shows no decrease in intensity in the green.

The heat of formation of gaseous hydrogen chloride from H_2 and Cl_2 is 22 Cal, corresponding to a wavelength 1295 $\mu\mu$, in the infra red. How far the spectrum extends to in the infra red is impossible to determine with the apparatus available, but it would appear surprising if, in fact, the spectrum were related to this figure of the heat of reaction, which is nearly certainly simply the nett sum of a number of elementary processes, and not associated with any one. There is no evidence of a band lying near 309 $\mu\mu$, corresponding to the heat of formation of hydrogen chloride from atoms; nor does the spectrum contain any features which can be identified with any of the emissions of chlorine produced by electrical excitation.

The origin of the emission actually observed remains to be considered. Neither hydrogen, nor chlorine, nor hydrogen chloride have been excited to emit radiation by mere heating to temperatures available in the laboratory, so that the spectrum is not simply the effect of the high temperature prevailing in the flame. That the hydrogen is probably not concerned in the emission is/

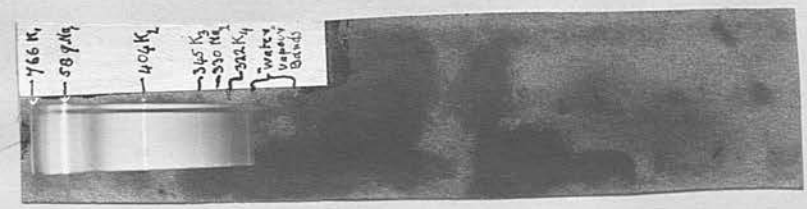
is suggested by the non-luminosity, under ordinary conditions of pressure, of the oxygen-hydrogen flame, in which the temperature will probably be at least as high as ~~the~~ in a chlorine-hydrogen flame of the same size. The general manner in which the emission may be produced will be considered later. (p.108)

---

(2) Flame Spectra of the Alkali Halides:

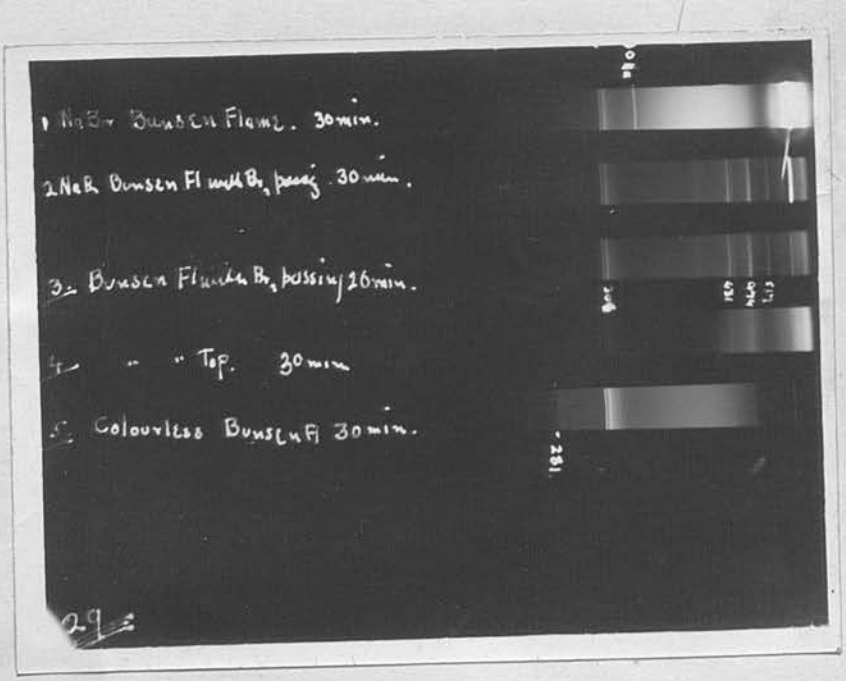
(a) Ordinary flame spectrum of sodium chloride. The shortest wavelength reported in the flame spectra of the alkali salts is 285 $\mu\mu$, that of the third member of the principal series of sodium. [Eder and Valenta, Beitrage zur Photochemie, p.87] With the object of extending the examination to the limit of the spectrograph used in this work, theultraviolet spectra of the bunsen flame coloured by the addition of alkali salts were photographed. Only the well known features of the spectrum appear, namely the first few members of the principal series of the metal, the continuous spectrum in the visible which has been known from the time of Bunsen, the "water vapour" bands at 308 and 281 $\mu\mu$, and no emission was recorded which could be attributed to a chemical radiation in the sense considered here. No trace of halogen emission was ever found. In an experiment to ascertain if the introduction of potassium iodide into the oxygen coal-gas flame caused the emission of the iodine line at 206.1 $\mu\mu$ an exposure of 2 hours was given, but no sign, either of/

FIG. 18



Spectrum of KI in Bunsen Flame.

FIG. 19.



Na Br Flame Spectra.

of the line, nor of the "reaction band" appeared. The photograph, reproduced in fig 18, shows the Ist four members of the principal series of potassium, as well as the first two of sodium, and incidentally shows that the bunsen flame coloured with sodium chloride is very far from being a source of "monochromatic light". Another attempt to observe the iodine line after 9 hour's exposure also gave a negative result.

(b) Flame Spectrum of Sodium Bromide in presence of Bromine: It was found by Mitscherlich that sodium chloride did not emit the D lines in the hydrogen-chlorine flame, nor in a bunsen flame containing hydrogen chloride. The doublet is produced by the return of the valency electron from a pair of orbits which it may occupy when the atom assumes a certain state of excitation, to the normal orbit of the unexcited atom. The absence of the lines in the presence of halogen might therefore be due to the robbing by the halogen of the valency electron of the sodium, with the production in the flame of Na^+ and Cl^-; the appearance of the electron affinity spectrum of the halogen might then be expected. To investigate the point, the spectrum of sodium bromide in a bunsen flame containing bromine was photographed. (fig. 19.)

(I) is the result of 30 minutes exposure to the simple sodiumbromide flame. The D lines show prominently, and thesecond member of the principal series, at

330/

330$\mu\mu$ also appears. The band degraded towards the red at 308$\mu\mu$ is the so,called water vapour band. The continuous spectrum beginning in the green and extending to beyond 300$\mu\mu$,, is also due to the salt.

(2) Bromine was now passed up the bunsen, The flame became elongated and faintly luminous, the upper part being coloured a livid yellowish green. The green cone was enlarged and intensified, and the Swan bands of carbon,emitted by this cone, are strong in the photograph. The yellow sodium light disappeared except in the immediate neighbourhood of the point at which salt aws introduced. The D line appears in the plate, but is much less intense than in (I); the times of the exposure and rate of introduction of the salt were the same in both cases. The sodium line at 330$\mu\mu$ has not appeared. The plate shows no sign of bands about any of the positions characteristic of the bromine vacuum tube spectrum, nor of the bands which can be correlated with the energy of reaction.

Two explanations of the supression of the D lines seem to be possible. There is no doubt now that the D lines are emitted by the sodium atom, and since they enormously exceed in intensity the other members of the principal series, and especially of the subordinate series of the arc spectrum, they must originate in atoms which are not fully ionised; if a large number of atoms is fully ionised, the return of the electrons is accompanied by the emission of the whole arc spectrum, including the principal and firstand second subsidiary series/ .

series, The flame must t hen contain neutral sodium atoms, which we may regard as produced by the dissociation of the salt.

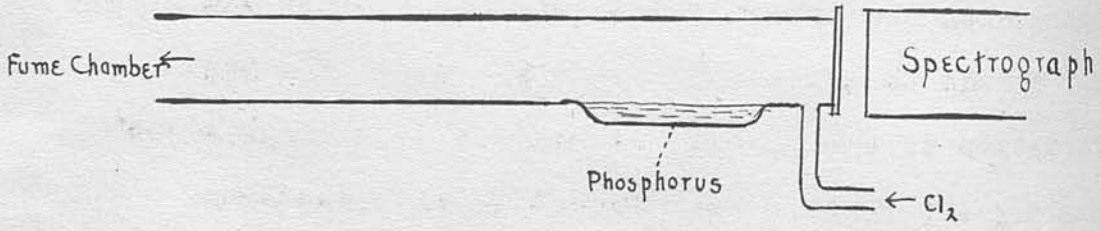
$$Na\ Cl = Na + Cl$$

That the dissociation follows this course rather then that leadingn to the production of ions, as in electrolytic dissociation, is indicated by H. A. Wilson's experiments on the mobility of theions in flames, [Phil. Trans. A. 192, 499, (1899)] in which it was found that the velocity of the negative ion greatly exceeded that of the positive. The negative ion must be the electron and not the heavy halogen ion; the actual ionisation in flames is probably produced by ionisation of some of the sodium atoms formed in the dissociation of the salt. If an excess of halogen atoms is present, the dissociation will be "thrown back" according to the mass law; at the temperatureof the flame, there will be a considerable concentration of halogen atoms, andthe equilibrium forced back in the direction of the undissociated salt.

The other possibility is that the electronegative halogen atom may remove the valency electron from the sodium, with the formation of Na^+ and Cl^- ions. The Na^+ would then be in a condition in which it could emit its spark spectrum, and as the fundamental lines of this spectrum are far in the ultraviolet, corresponding in fact to the L series in the X-ray spectrum of heavier atoms, they would escape detection by a quartz /

FIG. 20

REACTION BETWEEN Cl_2 AND P.



½ Natural Size.

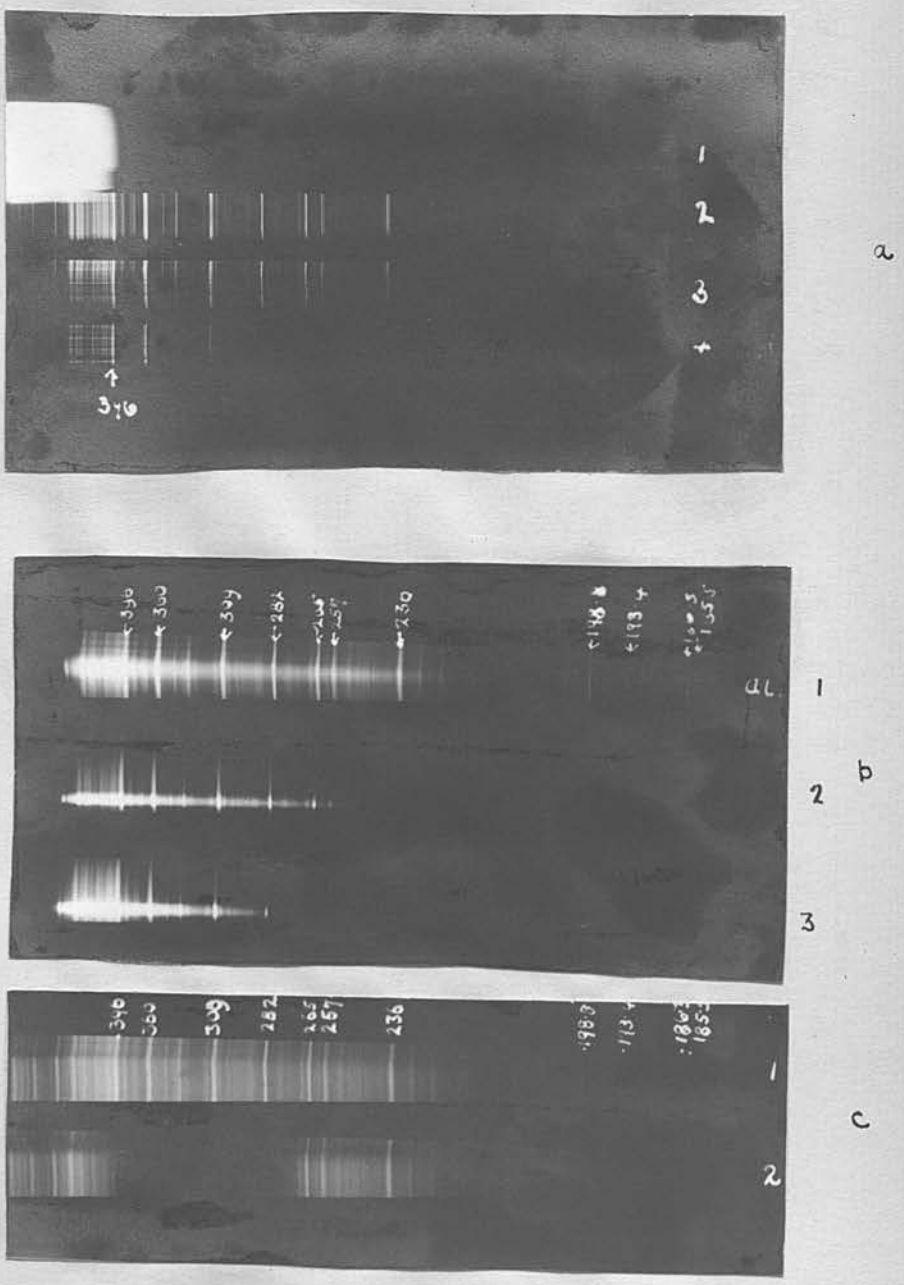
quartz spectrograph. Perhaps mobility measurements in a flame containing excess halogen might indicate if this process occurred, as the negative ions would then be negatively charged halogen atoms and would possess low mobility. The absence, however, of the electron affinity spectrum is some ground against this second hypothesis, and the more chemical explanation seems adequate to account for the suppression of the D lines.

3 The Reaction between Phosphorus and Chlorine.

The union of phosphorus and chlorine may take place with the emissionof light; the attempt was therefor e made to photograph the spectrum. The heats of formation of the phosphorus halides from their elements arehigh. (70 Cal. for formation of phosphorus trichloride from solid phosphorus and chlorine gas, 105 Cal. for formation of solid phosphorus pentachloride from its elements) indicating that any chemical radiation would be in the ultraviolet region. It is known that both the rapid and the slow oxidation of phosphorus may take place with the emission of bands in theultraviolet [Emeléus and Downey J.C.S.125, 249, (1924)] and it seemed interesting to ascertain if these bands were also emitted in thereaction with chlorine.

The apparatus used is shown in fig 20. A strong draught was employed to sweep away the products of reaction/

Fig 21.



a. 1. Spectrum of the P-Cl flame. 2 hr's exposure.
2 al spark
3. al spark
4. al spark through 1mm liquid PCl_3

b 1. al spark
2 +3 al spark through 2cm. PCl_3 vapour at 100° and 150° respe

c 1. al spark
2 al spark through 6 cm. Cl_2 at atmospheric pressure

reaction. The passage of a fairly vigorous current of dry chlorine over the phosphorus caused the latter to melt; it began to glow with a greenish light, and finally burst into a briliant white flame. The intensity of the flame could be regulated by adjusting the gas stream; and exposures were given to flames of various intensities, the times of exposure ranging from 15 minutes to 3 hours. In all cases the result was th e same; a continuous spectrum extended throughout the visible region and was cut off sharply at about 390 μμ. (Fig. 21.a.1).

A sudden limit to the spectrum might either be real, in which case it would be of theoretical importance, or it might be due to absorption by some of the substances present in the reaction. The absorption spectra of phosphorus trichloride and pentachloride and of chlorine were therefore observed. A layer of liquid phosphorus trichloride, 2 mm. thick transmits light to wavelength 300 μμ (fig. 21. a. 4) and the vapour will be at least as transparent. Phosphorus pentachloride vapour also is transparent to a region of considerably shorter wavelength than the limit of the phosphorus-chlorine reaction spectrum. (b) But it is seen that a layer of chlorine 6 cm. thick at atmospheric pressure absorbs strongly fromabout 393 to 282 μμ. (c) The limit of the chlorine absorption band at 393 is sharp, and coincides with the short wave limit of the phosphorus-chlorine spectrum, and there seems no doubt that it was the absorption/

absorption of the 2 cm of chlorine between the flame and the quartz window which caused the sudden stoppin the emission spectrum.

Calculations of the intensity of light transmitted through a layer of chlorine 2 cm thick, at atmospheric pressure, based on the phot ometric measurements of v.Halban and Siedentapf [Z.f.phys.Ch. 103, 71,(1923)] show clearly the strong absorption of chlorine in the near untraviolet. Table X gives the values of the extinction coefficient α, defined by the relation

$$I = I_o \times 10^{-\alpha t}$$

where I_o is the incident intensity and I the emergent intensity after passage through a layer t cm thick of the gas at atmospheric pressure, and the values of the fraction of the intensityabsorbed calculated from this equation for regions near the edges of the band. Values denoted by + are interpolated from v.Halban and Siedentopf's data.

TABLE X

Absorption of Chlorine (2 cm at atmospheric pressure)

λ ($\mu\mu$)	α	% Incident Intensity absorbed	λ ($\mu\mu$)	α	% Incident Intensity absorbed
405	0.1808	56%	280	0.335	79%
+ 390	0.40	84%	265	0.0556	23%
+ 380	0.63	95%	254	0.01085	7%
+ 370	1.00	99%			
366	1.233	99.5%			

These figuresshow very clearly the rapid increase in the absorption of chlorine in the near ultratiolet.

Chlorine/

Chlorine, however, would not suppress any considerable emission of wavelength shorter than about 270 μμ, and as the construction of the apparatus and the use of a strong draught to remove the products of the reaction seem to preclude the possibility of absorption by these, the conclusion appears necessary that in the reaction between chlorine and phosphorus there is no emission of radiation in the middle and further regions of the ultraviolet. Of the five ultraviolet bands reported by Emeléus and Downey in the light accompanying the oxidation of phosphorus, four, of wavelength 263, 253, 248 and 239 μμ, are in the region transmitted by chlorine, so that they appear to be absent in the phosphorus-chlorine flame.

4. Attempts to Detect Radiation at Low Pressures.

It seemed possible that the failure to detect chemical radiation in the experiments hitherto described might be connected with the relatively high pressure prevailing. If the radiating centre had a certain "life period", similar to that possessed by atoms which have been excited to a higher quantum condition than the normal, during which it could persist in the state of abnormally great energy in which it must exist at the moment of its formation, and if collisions with other molecules took place within this period, the energy might in some way be conveyed to these, and therefore/

therefore would not escape as electromagnetic radiation. If, as a first approximation, we assume that the "life period" of the active molecule is of the order 10^{-8} sec, the value of the period in which the mercury atom can exist in the excited $2p_2$ state, the number of collisions experienced in this interval by the molecule of an average gas, with a collision frequency of about 10^{10}, would be 100*, so that if direct transference of energy occurred, there would be little opportunity for any to reach the exterior as radiation proper to the reaction. Reduction of the pressure to about 0.01 atmosphere would prevent this possibility, if the value for the active period bears any relation to the truth.

The reaction studied was that between chlorine and the liquid alloy of sodium and potassium.

Preparation of Sodium - Potassium Alloy: 9 gm. of clean potassium and 2.5 gm. of sodium, which are approximately the proportions for the alloy of greatest fluidity, were introduced into a 100 c.c. distilling flask (fig.22) containing sufficient benzene to cover the metals. The neck of the flask fitted into a ground joint fused to a bent tube ground into the neck of the funnel D. A side tube with tap A was provided lest additional pressure should be required to force the alloy through the tap E in the subsequent experiment, but this was not required. The constricted

leading/

* In this calculation, the increased diameter of the excited molecule with its consequent decrease in mean free path and increase in collision frequency has been neglected.

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leading/

* In this calculation, the increased diameter of the excited molecule with its consequent decrease in mean free path and increase in collision frequency has been neglected.

leading tube of the distilling flask was connected to the oil pump through tap B, and through a receiver F, at -20° C, for the benzene, to the water pump. Between the filter pump andthe distilling flask was placed a large tube containing phosphorus pentoxide.

The benzene was distilled off under water pump vacuum, the tap to the oil pump being closed; the benzene was thus prevented form contaminating the oil of the pump. Immediately the ben zene was distilled, connection was made to the oil pump, and the pressure reduced to 0.001 mm. The metals in the distilling flask were kept molten for some time with the pump running; the flask was then sealed off at the constriction, and the liquid alloy passed through a copper gauze, which retained any film, to the funnel D, where it collected in a bright, mobile liquid.

The Reaction between Chlorine and the Alloy: This was carried out in a dark room, a feeble red light being employed when necessary. The dropping funnel containing the alloy was attached by rubber tubing flush with the end of a quartz tube fused into the silica reaction vessel R; this was mounted in a light-tight box provided with openings for t he inlet and outlet tubes, the outsides of which were coated with lampblack. All joints, other than that of the dropping funnel to the reaction vessel, were made by fusing or grinding.

The bulb A (fig. 23) was filled with solid chlorine and/

and the apparatus evacuated. A fast photographic plate (Imperial Special Rapid) was suspneded in contact with the reaction vessel. Top "a" was turned so as to break connection with th e pump; the temperature of the chlorine in A was maintained about the melting point (a pentane thermomet er being used) at which its vapour pressure is 8.9 mm, and the alloy allowed to enter the reaction vessel at the rate of one drop per second.

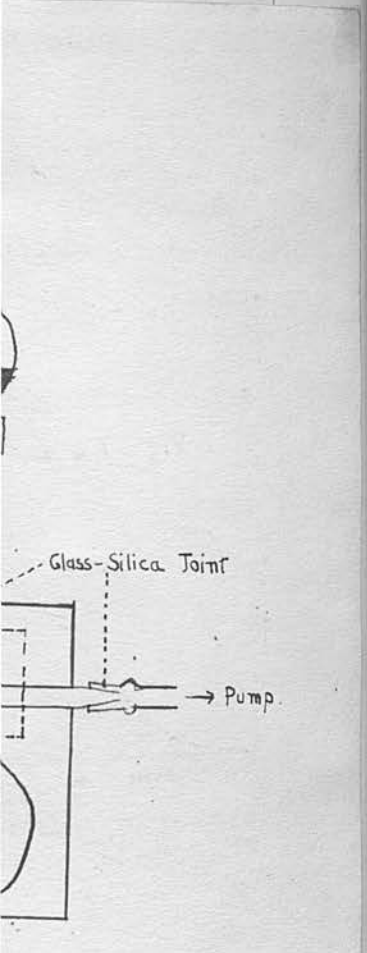
On developement the plate showed no trace of an image. Examination of the reaction vessel showed that considerable quantities of chloride were present, but evidently the combination under these conditions does not cause emission of appreciable amounts of radiation which can affect a photographic plate, or, at least, no appreciable radiation of this kind reaches the exterior.

5. The Reaction between Mercury and the Halogens at low pressure:

The reaction between the alkali metals and the halogens is much influenced by the presence of moisture, and, although it was obvious that considerable reaction had taken place in the last experiment, it was thought advisable to repeat the experiment with mercury, which Shenstone found, in a careful investigation [J.C.S. 71, 479, (1897.)] to be as rapidly attacked by very dry halogens as by the moist or incompletely dried gases.

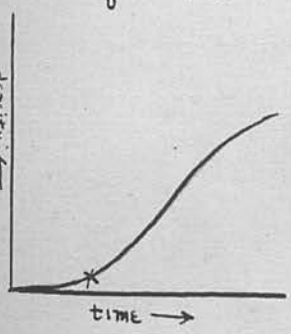
The/

The apparatus, modified slightly from that emp
ed before, is shown in fig. 24. The silica reaction vesse
was first evacuated by the oil pump; the reservoi
of two litres capacity, after having been washed
an hour by a rapid stream of chlorine passing thr
tap C, was filled with the gas. The chlorine wa
allowed to pass into the silica vessel through a
capillary tube permitting a leak of 0.5 mm. per m
the pressure being maintained in the reservoir by
of chlorine, the excess escaping through C. A f
photographic plate, sensitised by Wood's method*
J. 27, 379 (1908)] was placed in contact with th e
silica, opposite the jet.



* The principle of this method of sensitising p
is as follows. The relation b
the density of a negative and t
of exposure is shown in fig 24a
finite time must elapse before
, becomes perceptible, and, initi
increase in density with time o
is very slow. By a previous ex
to weak light, Wood brings thep
a condition represented by the
X, in which the density increas
approximately proportionally wi
time. The efficacy of the pro
with the plates used here was shown by the effec
2 seconds exposure to the iodine spectrum of a p
one half of which was sensitised by 3 second's
exposure at 2 metres distance from the luminous
of a bunsen flame. On this portion the 206 μμ lin
ed distinctly, while in the unsensitised part, t
exposure produced by a scarcely visible effect.

Fig. 24 a

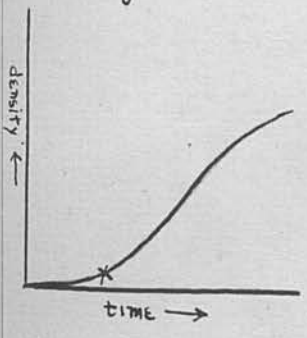


The/

The apparatus, modified slightly from that employed before, is shown in fig. 24. The silica reaction vessel was first evacuated by the oil pump; the reservoir B, of two litres capacity, after having been washed for an hour by a rapid stream of chlorine passing through tap C, was filled with the gas. The chlorine was allowed to pass into the silica vessel through a capillary tube permitting a leak of 0.5 mm. per minute, the pressure being maintained in the reservoir by a stream of chlorine, the excess escaping through C. A fast photographic plate, sensitised by Wood's method* [Astrop. J. 27, 379 (1908)] was placed in contact with the silica, opposite the jet.

* The principle of this method of sensitising plates is as follows. The relation between the density of a negative and the time of exposure is shown in fig 24a. A finite time must elapse before density becomes perceptible, and, initially, the increase in density with time of exposure is very slow. By a previous exposure to weak light, Wood brings the plate to a condition represented by the point X, in which the density increases approximately proportionally with time. The efficacy of the procedure with the plates used here was shown by the effect of 2 seconds exposure to the iodine spectrum of a plate, one half of which was sensitised by 3 second's exposure at 2 metres distance from the luminous tip of a bunsen flame. On this portion the 206 $\mu\mu$ line appeared distinctly, while in the unsensitised part, the same exposure produced a scarcely visible effect.

Fig. 24 a



The/

The plug of chloride which tended to form at the jet was removed by thepressure of mercury when the dropping tap was opened wide, after which a continuous stream of very fine droplets of mercury was allowed to enter the atmosphere of chlorine. The gas was absorbednearly as fast as it entered, so that no rise in pressure occurred, but in order to ensure a low pressure the pump was occasionally run for a few minutes. In this way, in the course of two hours, 250 c.c. (3,400 gm.) of mercury were run in. To permit the observation of the reaction, the dark box was provided with a movable shutter; no visible radiation was detected by therested eye in a dark room. The plate after development showed no image.

The heat of formation of mercuric chloride is 53.3 Cals., so that the conversion of I gm. of mercury to this chloride leads to the nett evolution of 0.26 Cal. or 1.1×10^{10} ergs; since, according to Eder, [Handbuch der Photographie, p.34, (1906)] one erg. of the total radiation of a luminous source, such as is used in photometry, will produce a distinct impression on a photographic plate, even although not more than I % of the energy is photographically effective, it is evident that in this reaction, any emissi on of energy as radiation can only be an infinitesimal part of the total energy emitted.

6 The Reaction between Sodium and Iodine at Low Pressure/

Pressure: The experiment with chlorine and sodium-potassium alloy showed that no appreciable quantity of radiation was produced in the reaction at ordinary temperature and at low pressure. It was observed, however, that iodine at low pressure, led from a tube through which a glow-discharge was passing, over metallic sodium, heated just above the melting point, caused the emission of the D lines, and it was afterwards found that the passage of the discharge was not a necessary condition for the production of the radiation. The spectrum of the glow was therefore photographed in order to determine if the sodium radiation were accompanied by any emission in the ultraviolet. The wavelengths corresponding to the possible reactions are in the region within the range of the spectrograph; for example, the heat of formation of solid sodium iodide from solid sodium and solid iodine is 69Cal; the value from gaseous sodium and gaseous iodine will therefore be 69Cal.+(Heat of sublimation of Sodium +Heat of sublimation of iodine) = 69 + 21* + 4.5† = 94.5 Cal., equivalent to a wavelength of 300 $\mu\mu$; the heat of formation from sodium vapour and atomic iodine will be 94.5 +(heat of dissociation of I_2) = $94.5 + \frac{35}{2}$ = 112 Cal., equivalent to a wavelength of 250 $\mu\mu$ while the heat of formation from ions, is, according to the theory of the crystal lattice,‡ about 144 Cal., corresponding to $\lambda = 200\,\mu\mu$.

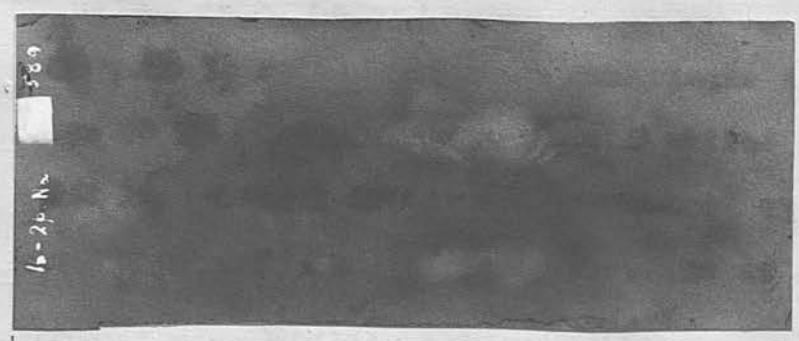
A clear quartz tube, 1 cm. in diameter was blown at one end to form a short focus converging lens; near this was fused a silica side tube containing a few crystals/

* † ‡ See foot note on p.87.

crystals of iodine. A piece of clean sodium was placed in the tube, which was then evacuated by the oil pump; the pressure of iodine vapour would be the saturation pressure at room temperature (15° C), 0.13 mm.
The pump was kept going th roughout the experiment, so that a continuous stream of vapour at this pressure passed over the metal. The tube was placed in a small asbestos furnace provided with a thermometer. At room temperature, no radiation was visible near the metal, but on warming it just above the melting point, a yellow glow became visible over the sodium, which became very bright when the temperature of the oven was 130° C, and persisted even when the temperature was lowered to 95°.
A small bunsen flame, ½ inch high, placed 8 inches below the tube, kept the metal molten throughout the experiment. The yellow glow moved to a position between the source of iodine vapour and the metal; the front of the glow, where the halogen first met the sodium vapour, was greenish; beyond the heated metal, towards the pump was a steady ring of the same glow. Visual examination showed this glow to be continuous, with scarcely a trace of D line. The bunsen flame having been extinguished, the yellow glow became feebler, the light became greenish; finally, only the surface of the metal glowed with a blue colour; and, after further cooling, no visible radiation was emitted.

The glow was photographed end on with a panchromatic plate/

FIG. 25



Spectrum of the glow in the reaction between Sodium and Iodine. (very wide slit.)

plate sensitised by Wood's method. The tube was filled wit h sodium several times, and a total exposure of three hours made. The D line alone appeared on the developed plate. (fig. 25). Five grams of sodium were used in the experiment; the conversion of only 0.I gm. of this to iodide would cause evolution of 60 cal. or 2.5×10^9 ergs, so that no appreciable fraction of the energy can be emitted as radiation. There is, moreover, no stimulation of theresonance line of iodine. On the other hand, the excitation of the sodium resonance line is a result of the reaction, since many experiments, in which sodium has been distilled in vacuo and the vapour heated to a greater degree than in this experiment, have shown that under these conditions no yellow light is emitted.

Haber and Zisch [Zeit.f.Physik, 9, 302, (I922)] performed an experiment similar to the above, in which halogens mixed with 4 to 5 times their volume of nitrogen, (the total pressure being one atmosphere) reacted wit h sodium vapour. The lowest temperature at which the radiation was observed in this case was 350° — 360° C (for chlorine) which is considerably higher than that employed in th e experiment described above; moreover they observed the spectrum through a mica window, which is opaque beyond $\lambda = 300 \mu\mu$. (The light of a powerful aluminium spark was completely cut off below $300 \mu\mu$ by a sheet of clear mica 0.07 mm. thick) Only the D line

and/ * Bajans Verh,d,deut,Phys.Ges.2I,7I4,I I quotes 2I Cal. as heat of sublimation of K; I have assumed that that of Na will not be very different.

+ Landolt-Bornstein 3rd.Edt. p.1475

* Born Ver h.d.Phys.Ges. 2I, I3, I9I9.

and the continuous visible emission are reported by those authors.

An experiment with mercury and iodine vapour, similar to that with sodium, showed that in this case the reaction, when carried out at temperatures of 100 - 200°C, was unaccompanied by the emission of radiation.

General Discussion.

The experiments have shown that in the formation of heteropolar compounds, under no condition examined does an appreciable amount of light capable of affecting a photographic plate reach the exterior. The question concerning the manner in which the energy made available in a reaction escapes/therefore remains unanswered. At the instant of its formation, a molecule must possess the energy which is ultimately emitted if it is to have a permanent stability and the problem is, in what way the loss of energy takes place. The other question which arises from this work is that of the origin of the radiation which is actually emitted in some chemical reactions; and it will be shown that this is very likely a part of the general problem of the elementary emission process.

The activated product of a reaction could lose its energy in the following ways.

(1) The energy might be given up in the form of radiation which cannot affect the photographic plate (infra red radiation) or as visible or ultraviolet radiation which is in some way prevented from reaching the exterior.

(2) The energy might be passed on by collision to unactivated molecules of the reactants, or to resultant molecules which have already lost their energy of reaction.

(3) The energy might be lost in some way not definitely known.

We/

We may first consider the latter possibility. Polanyi indeed [Z.f.Physik.3,31,(1920)] seems to consider that an activated molecule formed in chemical reaction loses its energy in a special way. His argument is: the emission of radiation is due to a quantum jump which an electron makes in an atom, with which is coupled a quantum jump in the ether. The loss of energy in the first jump covers that required for the coupled jump in the ether. Similarly, a quantum jump in a material system might be coupled with a quantum jump in another material system; thus the return of an activated molecule to its normal condition might necessarily be coupled with the transition of another inactive molecule to an active state. It is not clear how the coupling is effected; if in the process of collision, the matter is included in the second possibility; if it does not occur in collision, nor with the ether as intermediate, it is necessary to postulate some unknown method of energy transfer. As will appear, the known processes by which transfer of energy takes place seem adequate to account for the dissipation of chemical energy.

Consider now the possibility of the elimination of the energy of reaction as radiation. If any of the components of the reacting mixture is strongly absorbing, it might happen that most of any radiation emitted in the reaction would be retained within the system. Such/

Such a consideration, however, seems inadequate to explain the absence of the emission of radiation in any of the reactions dealt with here. In the experiments on the hydrogen-chlorine flame, the arrangement was such that there would be practically no unactivated chlorine present at any instant in a condition to absorb. Hydrogen is quite transparent up to a region in the extreme ultra violet; the photographs of Coehn and Stuckhardt [Z.f.Phys.Chem. 91, 737 (1916)] show that hydrogen chloride is transparent to at least 220 $\mu\mu$. Again in the experiments at low pressure with sodium-potassium alloy, and with mercury, the jet at which reaction took place was not more than I cm. distant from the walls of the quartz vessel, so that the absorbing layer would only be one of chlorine, I cm. thick, at $\frac{1}{100}$ of an atmosphere. The fraction of the light intensity which disappears in such a layer can be calculated from the equation $J = J_0 \times 10^{-\varepsilon c d}$ where ε is the extinction coefficient thus defined, c the concentration in gm.mols. per litre, d the thickness of the absorbing layer in cm. and J and J_0 the emergent and incident intensities respectively. At $\frac{1}{100}$ atmosphere, $c = \frac{1}{22.4 \times 100} = 0.000446$: for λ 334 $\mu\mu$, near the maximum of the chlorine absorption band, $\varepsilon = 65.5$ [v.Halban and Siedentopf. Z.phys. Chem. 103, 71, (1923)] whence $J/J_0 = 0.975$, so that even here the loss in intensity is only $6\frac{1}{2}\%$, and for other wavelengths it is still smaller/

smaller. In the experiments with sodium and iodine vapour, the radiation would have had to penetrate a layer about 12 cm. thick of iodine at 1/10 mm. Coehn and Gruckhardt found that a layer of iodine vapour 0.4 cm. thick at ½ an atmosphere was transparent down to wavelength 224 μμ; if Beer's law applies, the corresponding thickness at 0.1 mm. is about 2000 cm. so that no appreciable absorption could have occurred in the experiment; besides, direct experiments has shown that the whole iodine emission spectrum down to λ 200 μμ is not appreciably weakened after traversing 30 cm. of iodine vapour at 0.1 mm. pressure at room temperature.

There is the possibility that a radiation emitted in a reaction might be absorbed by molecules which had not reacted, to be re-emitted by the latter as resonance or fluorescent radiation, as is exhibited, in the simplest case, by metallic vapours exposed to the light of the first line in their principal series. If this process occurred in chemical reactions, light, which otherwise would originate sharply at the seat of the reaction, would be diffused through a greater volume, and the subsequent re-emission in all directions would lead to a diminution in the intensity of the light incident on the photographic plate; but not, if the original intensity were at all considerable, to its suppression. If, however, the re-emission took place as infra red radiation, it would escape detection by the plate, so that this possibility is not entirely excluded. On this point, and also concerning the possibility/

possibility of the primary emission of energy in several small quanta corresponding to infra red radiation, the experiments here described give no evidence.

The observation that no appreciable amount of ultraviolet radiation is emitted in chemical reactions, is supported by evidence provided by experiments performed with an entirely different object, namely by those intended to ascertain whether ionisation is a general result of chemical processes. It seems certain that, with the exception of reactions between the halogens and the alkali metals at low pressures where fairly large ionisation has been detected,* reactions do not take placewith marked ionisation. The latest worker on the subject, indeed, Brewer, [Jour, Am. Chem. Soc. 46, 1403, (1924)] found that in all gas reactions which he examined, the oxidation of nitric oxide, and the decomposition of nitrogen pentoxide and of ozone, a very slight ionisation could be detected (one pair ions produced for 10^{13} molecules reacting.) If, however, reactions were accompanied by the emission of an appreciable amount of ultraviolet radiation, there would have been a large photoelectric effect at the electrodes in such experiments, so that there would be apparently/

* Haber and Just, Ann.d.Physik 33,411 (1909)
Zeit.f.Elektch. 16, 275, (1910)
Ann.d.Physik 36,308 (1911)
Zeit.f.Elektroch. 20,483,(1914)
Richardson Phil.Trans. A.222,1, (1922)
Bratherton Trans.Roy.Soc.A.105,468,(1924).

apparently a large ionisation in chemical reactions. The absnece of this indicates that short wave radiation is not emitted, in general, in chemical reactions.

Transference of Energy by Collisions: We may now consider the second possibility mentioned on p. 89 ; transference of energy by collisions. The most precise conceptions on this question have been formed chiefly from the physical side by Franck and his co-workers In 1913, Franck and Hertz showed that an atom may be raised to a higher quantum condition by collision with an electron possessing a kinetic energy equal to or greater than the energy required to effect the change, any surplus energy being retained as kinetic energy of the colliding particles. Thus, if mercury atoms are bombarded by electrons which have fallen through a potential drop equal to orgreater than 4.9 volts; when they possess the energy required to raise the optical electron of the atom from the normal orbit 1S to the orbit $2p_2$, the electrons on collision transfer sufficient of their energy to the atom to activate it to this condition. After a finite time, the electron in the mercury atom falls from the $2p_2$ to the 1S orbit, the difference of energy between the two conditions appearing as monochromatic radiation of wavelength 254 $\mu\mu$. The process is one of the conversion of the kinetic energy of an electron, through the stage of internal atomic energy, to ~~the~~ electromagnetic radiation. Such collisions have been called "Collisionsof the first kind".

Klein/

Klein and Rosseland [Z.f.Physik.4,46,(1921)] next showed theoretically that the maintenance of statistical thermal equilibrium in a system consisting of atoms possessing an equilibrium distribution of internal energy among the different stationary states and of free electrons with an equilibrium distribution of velocities, requires that collisions of the first kind should be compensated by collisions in which an excited atom gives up its energy of excitation to a slow electron; the kinetic energy of the electron is thereby increased and the atom assumes a atate of lower internal energy, without emitting radiation. The energy lost by the atom in its transition fromthe higher to the lower state, which would otherwise have appeared as radiation, is now retained within the system as increased kinetic energy of a free electron. Such a collision has been called a "collision of the second kind." The mathematical consideration of the question shows that the probability of such radiationless transfers of energy is very great when the velocity of the free colliding electron with reference to the atom is small, and Klein and Rosseland predicted that it might be possible under certain conditions to detect a suppression of the emission of spectral lines by the action of slow electrons on excited atoms.

Franck in a series of experimental investigations has extended this notion to collisions between excited atoms and normal atoms and molecules. In such a collision/

collision the energy of an excited atom may be transfered to a normal atom or molecule so as to increase the internal energy of the latter. If an excited atom A' collides with another atom B which requires less energy to raise it from its normal stat e to the first state of greater energy than A the normal atom A, the atom B may undergo a transition to the excited state B' at the expense of A', which assumes its normal condition A without emitting radiation, the excess energy of A' over B' appearing as kinetic energy of the colliding atoms. After a certain life period, B' will return to B with the emission of the radiation of the resonance line. In thsi way it appears the mercury atoms excited by the absorption of the mercury resonance radiation can give up their energy of excitation to thallium and silver atoms, raising them to a condition in which they can emit their resonance line. The well known green line of thallium is emitted when a mixture of thallium and mercury vapours is exposed to light from a mercury lamp, while thallium vapour alone is unaffected by this light. [Cario. Z.f.Physik. 10, 192, (1922); Cario and Franck, ibid, 17, 202. (1923).]

The spectra produced by Strutt and Fowler [Proc. Roy. Soc. 86A. 108 (1911)] by the passage of active nitrogen over various substances seem to be produced in the same way. These spectra are characteristic of the substance over which the nitrogen passes, and are produced whether the encounter causes chemical reaction or not. The active nitrogen is probably in a higher quantum/

quantum state than the normal, and on collision with other atoms or molecules, it may transfer to them its energy of excitation raising them to a condition in which they may radiate, wothout itself emitting radiation.

Again, the energy of excitation of an atom may be transferred to another atom or molecule and raise it to a condition in which it can enter into chemical reaction. The device employed in high vacuum technique of passing a heavy discharge to remove the last traces of gas may depend on this fact. By the passage of the current, certain atoms are excited, which on collision with molecules, may cause them to dissociate; the resulting atoms will then combine with the electrodes or the walls of the vessel, since, as the pressure is low enough for the mean free path of the atoms to be comparable with the dimensions of the tube, collision of the atoms with the walls or electrodes will be much more probable than collision between two atoms and consequent reformation of the molecule.

More definite evidence on the transference of energy of excitation to a molecule so as to cause its participation in a reaction is afforded by an experiment of Cario and Franck. [Z.f.Physik, II,161,(1922).] It was found that illumination of a mixture of mercury vapour and hydrogen at low pressure by the light of a mercury lamp was attended by a reduction in pressure; oxides/

oxides, as tungsten oxides, unaffected by hydrogen at ordinary temperatures, were quickly reduced. The conclusion was drawn that the mercury atom, excited by the absorption of the resonance line 254 $\mu\mu$ transfers its energy on collision to the hydrogen molecule, which then undergoes dissociation. The reduction of pressure would be due to the absorption of the atoms on the walls; while the reduction of tungsten trioxide by hydrogen atoms has been shown by Langmuir to occur at the ordinary temperature. The energy emitted when a gm. atom of mercury suffers a transition from the excited $2p_2$ to the normal IS state is 112 Cal., and the heat of dissociation of hydrogen is 84 Cal., so that excited mercury atoms can effect the change. This experiment, and also that on the excitation of thallium vapour to emission show that the transfer from the excited atom does not take place via radiation, since hydrogen is quite transparent to 254 $\mu\mu$, and in the experiments with thallium, excitation of the green line on exposure to mercury light occurs only when mercury vapour is mixed with thallium. Interchanges of energy between atoms and ether appear to be fundamentally different from those between atoms and electrons or excited atoms in that, in the first case, the transference takes place only if the quantum of radiant energy possesses one of a series of discreet values/

values, while in a second it can be effected if the energy available in the electron or excited atom has any value (within limits) above the definite value required for the change, any surplus remaining as kinetic energy of the colliding particles. A quantum of radiation containing a little more energy than that corresponding to the D line of sodium is quite as ineffective in causing the emission of the line as one containing too little energy, while an electron possessing a kinetic energy greater than the energy of the line would cause its emission.

Extension to Chemical Reactions: These physical results have been discussed at some length because they appear to throw light on the problem of the emission of energy in the elementary chemical processes; and moreover, there are indications, as is shown by the results of Norrish and Rideal [J.C.S. 125, 2071, (1924)] that the "critical increments" in a number of different sulphur reactions are multiples of a fundamental quantity, that the process of activation of a reactant, whatever its mechanism may be, which in many reactions appears a necessary preliminary to the change, is analogous to the physical excitation of atoms studied by Franck. It has been shown that no appreciable amount of the energy of reaction is emitted as ultraviolet radiation, although its emission in this/

this way seemed possible on the grounds of current hypotheses of chemical reaction and of the origin of radiation; further, Franck has shown that under certain conditions a radiationless transfer of energy can occur when the mechanical process in the atom, the fall of an electron from a high to a lower quantum orbit is the same as that which under other conditions leads to the emission of radiation; and the conclusion is forced on one that the molecules formed in a chemical reaction lose their energy of reaction by a process analogous to collisions of the second kind. The course of a chemical reaction may be formulated in this way. Two molecules interact, because, as we may say, the potential energy of the system in its condition of final resultants is smaller than that of the system in its condition of initial reactants. At the instant of their formation, the resultants must contain the energy the loss of which is the condition that the reaction should proceed.

This energy of reaction is not given up as ultraviolet radiation, at least, not down to pressures of about 0.1 mm. It is, we must suppose, dissipated by collision with molecules which have not yet reacted, or with molecules which have already lost their energy of reaction. These molecules receive an increase in energy, which they may use in a variety of ways. The process seems to be entirely analogous to that/

that of collisions of the second kind, and may be identical with it. The term collision of the second kind has been restricted to collisions in which one of the particles is an atom previously excited by the absorption of radiation or by ~~the~~ electron impact. For convenience, the process by which we may regard the energy to be eliminated from resultants which owe their activation to a chemical reaction, may provisionally be called a"collision of the third kind" the new term being introduced to signify that the process depends on chemical activation rather than that it differs essentially from the collisions of the second kind studied by Franck and his collaborators.

That there may be transference of energy from one molecule to another in a reacting system is a hypothesis put forward by several investigators. Even before the formulation of Einstein's Photochemical Equivalence Law, Stark appears to have been one of the first to introduce the idea in order to explain photochemical sensitisation, in which a non light sensitive substance is caused to undergo reaction on exposure to light when mixed with another substance which absorbs the the particular light concerned, the latter substance being recovered unchanged at the end of the reaction. [Phys.Zeit. 9, 898 (1908).] He proposed that a molecule of the sensitiser, having absorbed a quantum, can on collision with a molecule of the other kind, raise the latter/

latter to a condition in which it may react.

Elimination of Heat in Chemical Reactions: The process producing this is analogous to a collision of the second kind causing an increase in the kinetic energy of a slow electron. The active resultant, on collision with molecules which have not yet reacted, or which are already deactivated, transfers its energy of reaction to these and increases their kinetic energy; the temperature of the system then rises. This appears to be the way in which the energy of reaction is ultimately dissipated; if any other method of transfer lasted over a long period, the assumption that the change in total energy in a reaction is measured by the calorimetrically measured heat of reaction at constant volume would require reconsiderations.

Production of Light in Chemical Reaction: In a number of chemical reactions, light is emitted which cannot be ascribed to a purely temperature effect; the emissions observed in the reactions studied here are cases in point. Where solid reactants are formed in a region of high temperature, as in the luminous bunsen flame, the emission is probably very largly simply temperature radiation from the solid particles, but such an explanation cannot account for the chlorine-hydrogen flame, where no solid particles are present, and which emit light at temperatures at which none of the reacting or resulting gases have been caused to radiate/

radiate by simple heating. We may consider in particular the light emitted in the reaction between sodium and iodine at low pressure. A quite intense yellow glow was produced when the temperature of the oven containing the reaction tube was 130°C, and it was possible to observe the glow when the temperature was as low as 95°. The temperature of the glow would be somewhat higher, but when the small amount of reaction taking place is considered, we may consider 200° as well beyond the upper limit.

(Continued on next page)

The number of sodium atoms with an electron in the 2p orbits (in which condition they can emit the D lines) in equilibrium with normal atoms at 200°C can be calculated from Nernst's equation for the relation between equilibrium constant and the heat of reaction, as applied by Saha to the ionisation of gases [Saha Phil.Mag. 40, 478, (1920).] The "approximation form" of Nernst's well known equation is,

$$\log K_p = \frac{\sum p'^m}{\sum p^n} = \frac{U}{4.571T} - \sum \nu 1.75 \log T + \sum \nu C.$$

where K_p is the equilibrium constant with reference to partial pressures,

$\sum p'^m$ and $\sum p^n$ are partial pressures of resultants and reactants raised to the appropriate powers.

U is the heat developed in the reaction.

$\sum \nu$ is the difference between the number of molecules on the two sides of the chemical equation.

$\sum \nu C$ is the sum of the chemical constants of reactants — sum of chemical constants of resultants.

If we consider normal and excited atoms to be thermodynamically distinct forms, this equation can be employed to determine the equilibriun in the reaction $A = A'$ where A' is an excited atom. $\sum \nu = 0$; since the chemical constants of monatomic gases depend only on their masses and since the masses of the two forms are the same (the very slight increase of mass of A' over that of A associated with its greater energy content being, of course, neglected) then $\sum \nu C = 0$, so that

$$\log \frac{p'}{p} = \frac{U}{4.571\,T}.$$

If/

If p' is small compared with p, we can put p equal to the total pressure, and $\frac{p'}{p} = x$, the fraction of atoms in the excited condition.

Thus, $$\log x = \frac{U}{4.571T}.$$

For sodium, the resonance potential is 2.1 volts, which is equivalent to 48,500 cal. This is the heat absorbed in the reaction $Na = Na'$, so that $U = -48,500$.

$$\log x = -\frac{48,500}{4.571 \times 473}$$

$$x = 3.7 \times 10^{-23}$$

The number of gaseous molecules per c.c. at atmospheric pressure is 2.7×10^{19}; so that, even at atmospheric pressure there is only one excited atom per litre at 200°C. Even at 800° absolute, above a red heat, the number of excited sodium atoms per c.c. at atmospheric pressure is only 10^6, or at 8 mm., the vapour pressure of sodium at this temperature, 10^4 per c.c. The emission of light observed in the reaction cannot be caused simply by the temperature of the region of reaction. The only source seems to be the energy made available in the reaction, which is communicated to the sodium atoms in some other way than as thermal energy. The production of light in chemical reaction between gases seems to be due to collisions of the third kind, in which the activated resultants, if they have energy equal to or greater than that required to raise reactants or normal resultants to a state in which they can emit radiation, pass

on/

on their excess energy to the latter and assume themselves a state in which they may have a permanent existence.

The conclusion that the light emitted in some chemical reactions is, so to speak, a by-product, has been previously arrived at by Haber and Zisch [Z.f. Physik, 9 ,302,1922] who examined the luminosity attending the interaction of sodium vapour with chlorine at a total pressure of one atmosphere, and at temperatures of 350° to 500° C. Kautzki and Zocher [ibid. 10,192, 1922] also found that the spectrum of the chemiluminescence accompanying the oxidation of certain unsaturated silicon compounds was identical with the fluorescent spectrum emitted in the absence of reaction, and concluded that the chemiluminescence, like the fluorescence was produced by molecules not in the process of reaction. Later, Kautzki and Neitzke [Z.f.Physik, 31,60, 1925] described experiments in which the oxidation of these silicon compounds caused dyes such as rhodamine, with which they are mixed to emit the light of their fluorescent spectra, a phenomenon which appears analogous to the excitation of the thallium spectrum by activated mercury atoms.

The condition for the emission of light by this reflex process will be that the energy possessed by the activated molecules should equal or exceed that required to raise the normal molecule with which it collides/

collides to one of the definite quantum states. The energy required to raise the optical electron of the sodium atom from the normal to the 2p orbit is 48.5 Cal; the energy made available in the reaction between the gaseous sodium and gaseous iodine is 94.5 Cal., hence the excitation of the sodium. We may picture the processes which cause the emission of the D lines. A sodium iodide molecule has just been formed and has not yet lost its energy of reaction. In this condition it collides with a sodium atom which has not participated in the reaction; a transfer of energy from the salt molecule to the sodium atom takes place; the internal energy of the sodium atom is increased by 8×10^{-20} cals.; the atom adjusts itself to its new energy condition in that the valency electron springs from its original orbit to that of next higher energy, where it persists for 10^{-8} seconds; it then rerurns to its original orbit with the emission of its excess internal energy as yellow light. The portion of the energy of reaction of the salt molecule which has not gone to increase the internal energy of the sodium atom is distributed between the colliding particles so as to increase their kinetic energy.

On the other hand, the energy required to raise the iodine atom from its normal condition to that in which it can emit the resonance line at 206 $\mu\mu$ is 138 Cal.per gm. atom, a quantity greater than that possessed by the nascent salt molecule. The line will therefore not be emitted/

emitted in the reaction , as was found experimentally to be true. Again, the heat of formation of solid mercuric iodide from mercury and iodine vapours is 38.8 + 12.4 = 51.2 Cal. (value for formation of solid HgI_2 from liquid mercury and iodine vapour + latent heat of vaporisation of mercury;) the energy required to cause the emission of the mercury resonance line at 2537 $\mu\mu$ is 112 Cal., hence the non emission of the line in chemical reaction.

In the hydrogen-chlorine flame it is probably the chlorine which gives rise to the emission, since the absence of absorption by hydrogen and hydrogen chloride in the visible and near ultra violet indicates that the normal molecules of these substances are incapable of undergoing any quantum change requiring an amount of energy corresponding to frequencies in these regions. Chlorine, however, has a complicated band absorption spectrum in the visible and long wave ultraviolet, so that it is capable of responding to amounts of energy corresponding to this region. That the emission spectrum produced in the flame is continuous may be due to the high pressure; the broadening of spectral lines of high pressure is a well known phenomenon.

Ionisation in Chemical Reactions: The excitation of an atom to a state in which, it can emit its resonance line is a stage towards its complete ionisation, so that, if the energy change in a reaction is sufficient, the activated resultants might be expected to cause ionisation of molecules or atoms with which they collided. The ionisation energy of gases is very high/

high, (117,000 cal. for the sodiumatom, one of the most readily ionised) so that much ionisation is not to be expected in a purely gaseous reaction; and, in fact, the ionisation in gaseous reactions is very small. It is, indeed, difficult to see how the energy available in the chemical reaction could cause the ionisation in the reactions studied by Brewer (p 93.) since the energy of ionisation of gases like NO, O_2, etc., although unknown, are practically certainly greater than any amount of energy made available by chemical means. Most compounds studied, e.g. ether, benzene, toluene, have ionisation potnetials of about 10 volts, corresponding to an energy of ionisation of 230,000 cal. In no ordinary chemical reaction are such amounts of energy liberated. If, however, we postulate a statistical distribution of the atoms and molecules among the different states of internal energy, analogous to the Maxwellian distribution with respect to velocity, a certain small fraction of the molecules will be more or less advanced on the way to ionisation, and might be completely ionised on collision with active resultants. There is also the possibility of direct ionisation in more than one step. The work necessary to raise an electron from a solid metal is much less than that requiredfor gases; it corresponds to the threshold frequency in the photoelectric effect, and there is no /

no difficulty in accounting for ionisation when solid metals are present. According to this explanation of chemical ionisation where metals are present the process must resemble that occurring in the thermionic effect; and Richardson has found that the characteristic current-voltage curves in the reaction between sodium-potassium alloy and the halogens resembles that of the thermionic effect, rather than that of the photoelectric effect. [Phil.Trans. A.222,1922.]

Photochemical Sensitisation: This process also receives a general explanation in terms of collisions of the third kind. It is possible to cause a substance insensitive in itself to light of a given wavelength to undergo reaction on exposure to this light if a second substance is present which absorbs the light. This is the principle on which depends the possibility of making a photographic plate whcih is sensitive to all colours. Silver bromide does not absorb red light appreciably and a photographic plate is therefore insensitive to red; but if silver bromide grains are in very intimate contact with certain red-absorbing dyes, red light can affect the plate. We must assume that the actual amount of energy in the quantum corresponding to red light is sufficient to cause the change in the silver salt; the ineffectiveness of red is due to the absence of response of the salt to radiant energy of this sort. The dye, however, can absorb quanta of light containing this amount of energy/

energy; the molecules of the dye are thereby raised to state of greater energy, and on collision with a silver bromide molecule, they may transfer to the salt their excess energy and themselves resume their normal state. The silver bromide molecule has now received in collision the amount of energy required to effect the change which it could not pick up directly from quanta of radiation containing this same amount of energy. Weigert found that many gas reactions could be sensitised in a manner which can be explained similarly. [Ann.d.Physik,24,243,(1907)]. Ozone, for example, is practically unaffected by visible light; but exposure of a mixture of ozone and chlorine to visible light causes decomposition of the ozone, and quantitative study by Bonhoeffer [Z.f.Physik,13, 4,(1923)] has shown that two ozone molecules are decomposed for every quantum absorbed by the chlorine. The chlorine molecule, activated by the absorption of a quantum, on collision with an ozone molecule transfers to it sufficient energy to cause its dissociation; $Cl_2^{active} + O_3 = Cl_2^{normal} + O_2 + O$; the disappearance of the second ozone molecule is likely to be due to some secondary reaction such as $O_3 + O = 2O_2$.

Evidence from the Study of Chemical Kinetics:

Several investigators have postulated the possibility of the transfer of energy from activated to inactive molecules/

molecules in order to account for their individual results. Chapman and Underhill [J.C.S. 103, 500, (1913)] explain the inhibiting effect of oxygen on the union of hydrogen and chlorine by assuming that the by the action of the light an unstable active form of chlorine is formed, which by collision with oxygen on loses its excess energy, and though the details of the scheme which represents the mechanism of the reaction have been modified [D.L. and M.C.C.Chapman. J.C.S. 123, 3079, (1923)] the essential idea of the transference of energy from active to inactive molecules is retained.

Bodenstein [Z.f.Elektroch. 22, 57, (1916)] recognised that the hydrogen chloride at the instant of its formation must be in a condition of abnormal energy, and explained the high yield in the photochemical formation of hydrogen chloride over that to be anticipated on the basis of the equivalence law by supposing that the activated HCl molecule passes on its energy to chl chlorine and hydrogen molecules, bringing a greater number into reaction than that caused by the action of the light. Again, Baly and Barker [J.C.S. 119, 653, (1921)] attempt to explain the deviation of the behaviour of the hydrogen-chlorine reaction from that required by Einstein's law in essentially the same way. Quantitative expression has been recently to the conception of reflex activation as it enters into the velocity/

velocity of reaction by Christiansen and Kramers [Z. phys. Chem. 104, 457, (1923)] and by D.L. Watson [Proc. Roy. Soc. A (1925)].

Summary: The discussion can be summarised thus. The problem arises how the energy of reaction is emitted innthe elementary process. The experimental work described shows that, even down to low pressures, the energy in a number of vigorous reactions involving the formation of heteropolar compounds is not emitted as radiation which can affect a photographic plate. The study from the physical side of the behaviour of a system containing normal atoms and molecules and atoms in well defined states of excitation, shows that radiationless transfers of energy from excited to normal atoms occur, in which the internal mechanism of the excited atom suffers the same change as that which otherwise may give rise to radiation. The conception is extended to include the interaction of the excited molecules formed in a chemical reaction with normal reactants and resultants, and it is shown that on this basis a general kind of explanation can be given of such apparently unrelated phenomena as the emission of heatand of light in chemical reaction, ionisation in reactions, photochemical sensitisation, and certain cases of autocatalysis.

GENERAL SUMMARY:

(I) The object of this work was to ascertain if chemical reactions in general are accompanied by the emission of radiation representing the energy change associated with the reaction.

(2) The emission spectra of the halogens have been investigated. The essential similarity in type of the spectra of chlorine, bromine and iodine has been observed and a new line emission spectrum of iodine has been found. In all three halogens a band has been observed, of the form, and in the position of the predicted electron affinity spectrum. The spectrum of iodine has been produced by slow-electron impact and has been shown to be the same as that produced by high tension oscillatory discharges.

(3) It has been shown that iodine vapour is ionised by exposure to ultraviolet light of wavelength shorter than I85 μμ.

(4) The emission spectra of the halogen hydrides have been examined. They are identical with those of the corresponding halogen with the addition of the Balmer series of hydrogen. No emission has been observed which can be identified witha "reaction spectrum"

(5) A number of reactions have been examined, under various conditions of temperature and pressure, for a reaction spectrum. In no case has such an emission been found. The conclusion is drawn that the energy of/

of reaction is dissipated in the elementary process in some other way than as electromagnetic radiation.

(6) The consideration of physical results on the transference of energy between electrons and excited atoms, on the one hand, and normal atoms, leads to the co nclusion that the energy made available in chemical reactions is dissipated in collision with normal melecules, a conception which appears to account for, in a general way, the prediction of heat and of light in reactions, ionisation in reactions, photo-chemical sensitisation and certain facts of chemical kinetics.

The experiments on which this thesis is based have been performed in the Chemical Laboratories at King's Buildings in collaboration with Dr E. B. Ludlam.